MANGANESE-ACTIVATED ZINC BERYLLIUM GERMANATE PHOSPHORS[1]

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ABSTRACT

The luminescence emission of $(Zn, Be)_2GeO_4$:Mn phosphors at room temperature and near liquid nitrogen temperature is qualitatively similar to that of the $(Zn, Be)_2SiO_4$:Mn phosphors. In both the germanates and silicates, a green emission band is observed with low manganese and beryllium concentrations. Increase in the concentration of either of these two constituents causes the growth of a new band in the red region of the spectrum.

Certain differences in properties are noted, however, between the germanates and the silicates. The most important of these is the absence of any clear-cut "red" band in the low temperature emission of Zn_2GeO_4 containing large manganese concentrations. Corresponding Zn_2SiO_4 phosphors clearly show the red band.

The results of the emission measurements are discussed in the light of two hypotheses that have been proposed to explain the dependence of the luminescence of manganese on the nature and composition of the host crystal. It is concluded that the results are more in harmony with the "coordination" hypothesis (wherein color differences are related to differences in coordination number of the manganese) than with the "aggregate" hypothesis (wherein color differences are attributed to different configurations of Mn^{+2} in the crystal, i.e., singlets, pairs, triplets, etc.).

Data on the absorption and excitation of the germanates are also reported and discussed.

INTRODUCTION

It is well known that the luminescence color of divalent-manganese activated phosphors is restricted to the spectral range of green through red. Very few hypotheses have been advanced, however, to account for variation of the manganese luminescence within this range as a function of the nature and composition of the host crystal. It is recognized, of course, that the energy levels of the Mn^{+2} ion are strongly affected by the magnitude and symmetry of the electric fields to which the ion is subjected. Since these will vary from one host crystal to another, a corresponding variation in luminescence color is not surprising. General considerations of this kind, unsupported by detailed calculations, are of little value, however, in predicting the luminescence color of any particular manganese-activated material.

Of the few specific suggestions that have been proposed to account for the effect of the host crystal on the color of the manganese emission, the earliest, advanced by Linwood and Weyl (1), may be called the "coordination" hypothesis. From studies of the luminescence of manganese in a

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wide variety of oxygen-bearing glasses, these workers suggested that the green luminescence band arises from centers containing manganousion in fourfold coordination with oxygen, while the red emission is due to manganese coordinated with a greater number of oxygen ions, this number being six in the case of the glasses investigated. Since the number of oxygens surrounding a Si^{+4} ion in silicate glasses is four, the (MnO_4) group in such a glass resembles the (SiO_4) groups, which form the glass skeleton or "network"; Mn^{+2} in such (MnO_4) groups is, therefore, designated as "network forming" manganese. The higher oxygen coordination in glasses is achieved by cations like the alkalis or alkaline earths, which occupy the interstices of the (SiO_4) network, hence the more highly coordinated Mn^{+2} ions were termed "interstitial" manganese by Linwood and Weyl. It is to be emphasized that, in those crystals where the divalent host cation already has a sixfold coordination with oxygen, one obtains, by *substitution* of Mn^{+2} for the crystal cation, a (MnO_6) configuration,

TABLE I

	Ions at normal cation positions (C.N.* = 4)	Ions at interstitial positions (C.N. > 4)	Ions at Si^{+4} positions	Oxygen positions
Ideal crystal	Zn_{2-a-b}^{+2} Be_a^{+2} Mn_b^{+2}		Si^{+4}	O_4
Real crystal	Zn_{2-a-b}^{+2} Be_a^{+2} Mn_b^{+2}	$\Sigma\ (Zn^{+2}, Be^{+2}, Mn^{+2})x$	$Si^{+4(1-x)}$ $\Sigma\ (Zn^{+2}, Be^{+2}, Mn^{+2})x$	O_4

* Coordination number.

which should emit a red luminescence. The number of coordinated oxygen ions, rather than the interstitial or substitutional nature of the solid solution, is the determining factor for the luminescence color, according to this picture.

The "coordination" hypothesis was extended by Linwood and Weyl to certain crystalline inorganic phosphors, e.g., Zn_2SiO_4:Mn. Its further extension to the more complicated $(Zn, Be)_2SiO_4$:Mn system was attempted by Schulman (2, 3), who proposed a scheme to account for the known effects of beryllium and manganese concentrations on the luminescence of this phosphor. According to this scheme, the molar proportions and spatial distribution of the constituents of ideal *vs.* real $(Zn, Be)_2SiO_4$:Mn phosphors can be represented by the structural schemes in Table I.

In the ideal solid solution, there are, thus, no interstitial ions of any kind, and the divalent Be^{+2} and Mn^{+2} substitute only for the divalent Zn^{+2} in the crystal. Since Zn^{+2} in this crystal is fourfold coordinated with oxygen, the substituting Mn^{+2} would, likewise, have this anion environment, and the luminescence would be green. In the real phosphor crystals, it was proposed that the Zn^{+2}, Be^{+2}, Mn^{+2} are found in small part ($x << a$ or b) at other positions than the normal cation positions of the ideal

structure. It is assumed that, in the high temperature synthesis of the phosphor, some Zn^{+2}, Be^{+2}, or Mn^{+2} may replace some Si^{+4} in the (SiO_4) groups of the willemite structure. The deficiency of positive charges arising from the replacement of tetravalent Si^{+4} by divalent Zn^{+2}, Be^{+2}, or Mn^{+2} could be compensated either by omission of O^{-2} or by incorporating interstitial Zn^{+2}, Be^{+2}, or Mn^{+2}. It is assumed that the latter possibility is realized, and that the interstitial Mn^{+2} ions so formed, having coordination numbers greater than four, are responsible for the red band in (Zn, Be)$_2SiO_4$:Mn. From considerations of ionic sizes and polarization properties, it is clear why Be^{+2} should be so effective in replacing Si^{+4}, and hence causing the appearance of the red band. It is also clear that an increase in Mn^{+2} concentration should favor the appearance of the red band; for, once the need for interstitial ions is created by a $M^{+2} \rightarrow Si^{+4}$ replacement, the probability of an Mn^{+2} ion occupying the interstitial site, rather than a competing Zn^{+2} or Be^{+2} ion, will increase with increasing Mn^{+2} concentration.

Kroeger (4) has questioned this picture on the grounds that (*a*) the presence of interstitial Mn^{+2} ions in (Zn, Be)$_2SiO_4$:Mn is unlikely, and (*b*) that it does not account for the influence of the Mn^{+2} concentration. We cannot subscribe to the first objection, because the structures of Zn_2SiO_4 and Be_2SiO_4 are quite open (5) with ample room for interstitial ions, and because the high temperatures used in preparing these phosphors are conducive to structural disorders. Kroeger's second objection listed above is, likewise, hard to understand in view of the discussion given in the preceding paragraph.

Kroeger (4) has proposed another interpretation of the nature of the "red" *vs.* "green" emitting centers in (Zn, Be)$_2SiO_4$:Mn. He notes that the green emission band is predominant in this phosphor at low manganese concentrations, while high manganese concentrations favor the appearance of the red band. The same situation exists even in beryllium-free Zn_2SiO_4:Mn, in which, at -180 C, the red emission band appears when the manganese concentration is high enough. Kroeger suggests, therefore, that one kind of center consists of Mn^{+2} ions which have no other Mn^{+2} ions as near neighbors, while the other center consists of Mn^{+2} ions that have either one, two, or more other Mn^{+2} ions as near neighbors. A similar suggestion had been made by Maurer (6), as a possible explanation for the existence of the two red emission bands in $MgSiO_3$:Mn and Mg_2SiO_4:Mn found by Fonda and Froelich (7). The effect of Be^{+2} in calling forth the red emission in (Zn, Be)$_2SiO_4$:Mn is ascribed by Kroeger either to (*a*) the alteration of the crystal fields by the Be^{+2}, so that a singlet Mn then is in a field similar to that provided by a near Mn^{+2} neighbor in the beryllium-free phosphor, or to (*b*) the effect of Be^{+2} in promoting a clustering of Mn^{+2} ions into pairs, triplets, etc.[2]

[2] Another specific interpretation of the manganese activated luminescence in Zn_2SiO_4:Mn and (Zn, Be)$_2SiO_4$:Mn has recently been the subject of several papers (13, 14, 15). According to this view, the luminescent centers in the above phosphors are manganate and/or permanganate ions, while the simple Mn^{+2}-ion is not considered to be a luminescent center. Apart from the question of the physical significance of the representation of emission spectra by Gaussian curves, upon which this interpretation is based, we wish to point out the following objections to this picture. A large number of manganese-activated phosphors are known in which the presence

Since Zn_2SiO_4 and Zn_2GeO_4 are isostructural (8), the study of the (Zn, Be)$_2$GeO$_4$:Mn system reported in the present paper was undertaken in the hope of finding evidence in favor of one or the other of the two pictures proposed above, the "coordination" hypothesis or the "aggregate" hypothesis. This similarity in structure and chemical constitution, however, made it plain that qualitative similarities between the (Zn, Be)$_2$GeO$_4$:Mn and (Zn, Be)$_2$SiO$_4$:Mn systems were to be expected regardless of the validity of one or the other, or either, of the above-described hypotheses, and that only quantitative differences would have any significance in helping to choose between them. Included also in the work was a brief study of the absorption and excitation of the phosphors in order to gain some insight into these processes.

PREPARATION OF PHOSPHORS

Approximately 5 g batches of the phosphors were prepared by acetone milling of chemically pure ZnO, BeO, $MnCO_3$, and GeO_2 (10% excess over stoichiometric proportion) in half-pint porcelain pebble mills. After filtration and drying, the samples were air-fired in an electric furnace at 1150 C for 1–2 hours in 50 ml fused silica crucibles. Both higher and lower temperatures were tried in preliminary runs, and this temperature was finally chosen since it appeared to give complete reaction without too much undesirable sintering. Refiring at the same temperature had no apparent effect on the luminescence color or brightness. With some of the higher manganese samples initial firing was performed at 1050 C, resulting in a grey to brown phosphor. Refiring at 1150 C produced nearly white phosphors. Consideration was given to the possibility of silica contamination from the firing vessels, but close examination of the surface of the new smooth silica crucibles used showed no attack.

X-ray diffraction studies of the phosphors showed that solid solution of manganese in Zn_2GeO_4 takes place up to a Mn/Zn mole ratio of at least 0.5. Similar studies of the Zn_2GeO_4-Be_2GeO_4 system showed that there was limited solubility of Be_2GeO_4 in Zn_2GeO_4, increase of the Be/Zn ratio beyond about 0.2 producing no further contraction of the interplanar spacings. The incorporation of manganese in (Zn, Be)$_2$GeO$_4$ appeared to cut down the solubility of beryllium somewhat, a Be/Zn ratio of 0.05 representing approximately the limit of solubility at a Mn/(Zn + Be) ratio of 0.05. The situation here is, thus, qualitatively similar to that existing in the (Zn, Be, Mn)$_2$SiO$_4$ system (9, 10).

LUMINESCENCE EMISSION

Most of the Zn_2GeO_4:Mn and (Zn, Be)$_2$GeO$_4$:Mn samples were found to be excited quite efficiently both by radiation from a low pressure mer-

of manganate or permanganate is inconceivable. Among these are a number of halides, sulfides, and selenides. It is hard to imagine that manganate or permanganate exists in pure $MnCl_2 \cdot 4H_2O$ crystallized from solution, or in a NaCl:Mn or NaCl: (Pb + Mn) phosphor (16) made by precipitation from aqueous solution with concentrated HCl. These and other phosphors not only have emission spectra very similar to those found in the Zn_2SiO_4:Mn and (Zn, Be)$_2$SiO$_4$:Mn systems, but similar luminescence decay properties, as well. For these reasons, it seems to us hardly warranted to ascribe the luminescence of manganese-activated silicates to a special state and configuration of the activator that is attainable only in oxygen-bearing systems.

cury arc (2537 Å) and by that from a "blacklight" lamp (3300–4500 Å, peak at 3650 Å). For the measurements reported here, the former source was used exclusively, in combination with a Corning 9863 filter to remove most of the visible light.

The measurements were made photoelectrically as described previously (2), a single monochromator (B. & L. Laboratory Wavelength Spectrometer) being used here instead of a double monochromator, and a 931 photomultiplier instead of a nonmultiplying phototube. For the measurements below room temperature, the simple demountable Dewar flask shown in Fig. 1 was used. The phosphor was mixed with butyl acetate and the paste so-formed applied to the outer surface of the inner container, the butyl acetate then being evaporated by means of an infrared lamp. Frosting of the outer quartz tube was overcome by painting it with a thin layer of glycerol. As determined by a thermocouple mounted in place of the phosphor, the temperature, attained with this arrangement with a Pyrex inner container, was −60 C when a refrigerant of dry-ice-

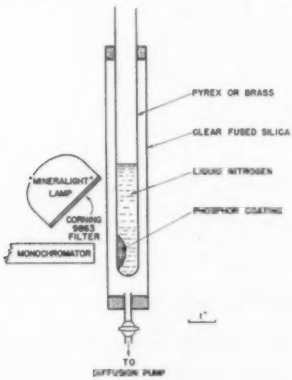

FIG. 1

acetone mixture was used, while with liquid nitrogen, the temperature was −150 C. With a metal inner tube, liquid nitrogen gave a temperature of −170 C. Comparison of the curves obtained with high manganese bearing Zn_2GeO_4:Mn ($\frac{Mn}{Zn} = 0.5$), at −150 and −170 C, showed that they were practically identical. The same was true of the emission of Zn_2SiO_4:Mn (Mn/Zn-.5) at −150 and −170 C. As a matter of convenience and ease of manipulation, our extended series of low temperature measurements was, accordingly, carried out with the Pyrex inner container.

The effect of variation in manganese concentration on the room temperature luminescence of Zn_2GeO_4:Mn is shown in Fig. 2. The emission consists of a band lying approximately between 4700 and 6200 Å, with a peak at 5300–5400 Å. On cooling the high manganese bearing phosphors to −60 or −150 C, an increase in brightness and a narrowing of the emis-

sion band is observed (Fig. 3). Fig. 4 shows the variation of spectral emission at −150 C of several Zn_2GeO_4:Mn phosphors, with emphasis on the preparations having a high manganese content; Fig. 5 gives the results obtained with comparable Zn_2SiO_4:Mn phosphors under the same conditions. In the latter case, our results agree qualitatively with those of Kroeger (10), who first showed the existence of a red band (peak at 6000–6100 Å) in the liquid air temperature emission of Zn_2SiO_4:Mn containing large manganese concentrations. We do not find the "green" and "red" bands in these high-manganese zinc silicates as well resolved as Kroeger did, but the growth of the "red" band is nevertheless clearly evident in our data. Under similar conditions, the Zn_2GeO_4:Mn phosphors show no such clear indication of the growth of a new emission band with increasing

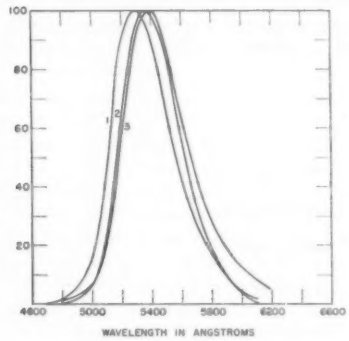

FIG. 2

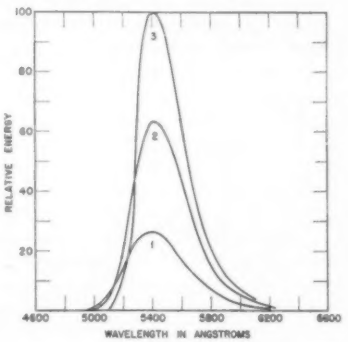

FIG. 3

FIG. 2. Spectral emission of Zn_2GeO_4:Mn at 25 C (peaks of all curves set equal to 100).

1. Zn_2GeO_4:0.005 Mn 2. Zn_2GeO_4:0.05 Mn 3. Zn_2GeO_4:0.4 Mn

FIG. 3. Spectral emission of Zn_2GeO_4:0.4 Mn at various temperatures
1. 25 C 2. −60 C 3. −150 C

manganese concentration, although a broadening of the "green" band and a shift of its peak to longer wavelengths is evident.

The effect of beryllium on the room temperature emission of zinc germanate is shown in Fig. 6 and 7, where the Mn/(Zn + Be) ratio is held constant at 0.025 and 0.05, respectively. It may be seen that the beryllium causes an apparent flattening of the emission spectrum, and a shift of the peak emission to longer wavelengths. In Fig. 7, there are some indications that the emission consists of two bands. With large excess of beryllium, there is a great decrease in efficiency. It should be noted that beryllium concentrations far above the solubility limit of Be_2GeO_4 in Zn_2GeO_4 have a considerable effect on the emission spectrum. In Fig. 8 is shown the effect produced on the room temperature emission characteristics by increasing the manganese concentration in a $(Zn_{1.6}Be_{0.4})GeO_4$ matrix. Low manganese concentrations in this beryllium-bearing matrix give rise to the green 5300–5400 Å band as in pure Zn_2GeO_4; increase in activator

concentration produces a broadening of the emission spectrum and a shift of its peak to longer wavelengths.

Fig. 9 and 10 give the spectral distribution of emission at −150 C of phosphors with Mn/(Zn + Be) ratios of 0.025 and 0.05, respectively, and with varying beryllium content. At this temperature, it is clearly seen that the emission of the beryllium-bearing phosphors consists of two bands, one in the green and the other in the orange-red region of the spectrum. The effect of beryllium is again quite marked, even at beryllium contents that exceed the solubility of Be_2GeO_4 in Zn_2GeO_4. Fig. 11 shows

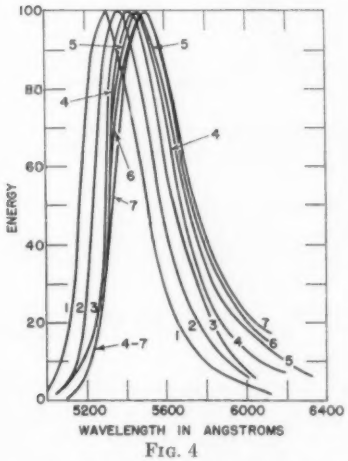

FIG. 4

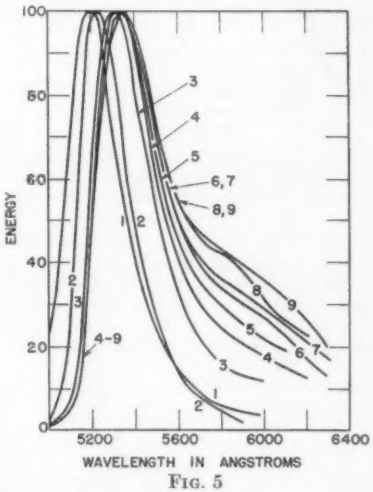

FIG. 5

FIG. 4. Spectral emission of Zn_2GeO_4:Mn phosphors at −150 C (peak of all curves set equal to 100).

1. Zn_2GeO_4:0.005 Mn
2. Zn_2GeO_4:0.01 Mn
3. Zn_2GeO_4:0.40 Mn
4. Zn_2GeO_4:0.5 Mn
5. Zn_2GeO_4:0.6 Mn
6. Zn_2GeO_4:0.7 and 0.8 Mn
7. Zn_2GeO_4:0.9 and 1.0 Mn

FIG. 5. Spectral emission of Zn_2SiO_4:Mn phosphors at −150 C (peak of all curves set equal to 100).

1. Zn_2SiO_4:0.005 Mn
2. Zn_2SiO_4:0.1 Mn
3. Zn_2SiO_4:0.4 Mn
4. Zn_2SiO_4:0.5 Mn
5. Zn_2SiO_4:0.6 Mn
6. Zn_2SiO_4:0.7 Mn
7. Zn_2SiO_4:0.8 Mn
8. Zn_2SiO_4:0.9 Mn
9. Zn_2SiO_4:1.0 Mn

how the emission of $(Zn_{1.8}Be_{0.2})GeO_4$:0.1Mn can be roughly resolved into two such bands, one similar to the emission of Zn_2GeO_4:Mn at this temperature, and the other peaking at about 5850 Å.

The apparent flattening and shifting of the room temperature Zn_2GeO_4:Mn emission spectrum upon the introduction of beryllium is due, no doubt, to the same effect that is observed at low temperature, the bands being completely unresolved at the higher temperature. The variation of the spectral emission with temperature is given in Fig. 12 for a $(Zn_{1.6}Be_{0.4})GeO_4$:0.1Mn phosphor.

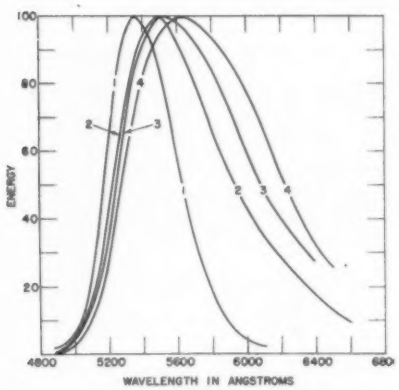

FIG. 6

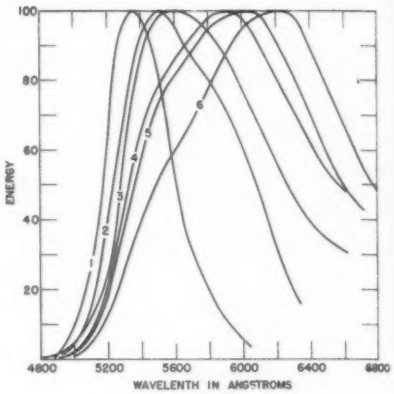

FIG. 7

FIG. 6. Spectral emission of $(Zn, Be)_2GeO_4$:Mn phosphors at 25 C (Mn/(Zn + Be) = 0.025 for all curves. Peak of all curves set equal to 100. Actual approximate relative peak heights: 1 = 100; 2 = 70; 3 = 50; 4 = 30).

Be/Zn

1: 0.0 2: 0.25 3: 0.43 4: 1.5

FIG. 7. Spectral emission of $(Zn, Be)_2GeO_4$:Mn phosphors at 25 C (Mn/(Zn + Be) = 0.05 for all curves. Peak of all curves set equal to 100. Actual approximate relative peak heights: 1 = 100; 3 = 50; 4 = 23; 5 = 10; 6 = 4).

Be/Zn

1: 0.0 2: 0.05 3: 0.11 4: 1.0 5: 1.5 6: 2.33

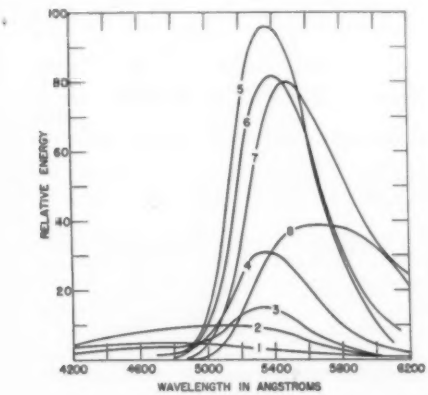

FIG. 8

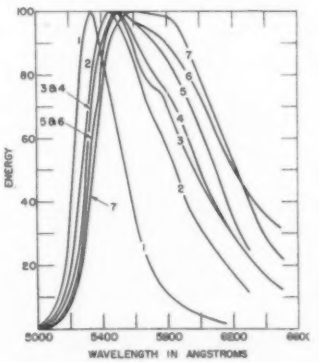

FIG. 9

FIG. 8. Spectral emission of $(Zn, Be)_2GeO_4$:Mn phosphors at 25 C (Be/Zn = 0.25 for all curves).

Mn/(Zn + Be)		*Mn/(Zn + Be)*	
1. 0	3. $2.5(10^{-4})$	5. $2.5(10^{-3})$	7. $2.5(10^{-2})$
2. $5(10^{-5})$	4. $5(10^{-4})$	6. $5(10^{-3})$	8. $5(10^{-2})$

FIG. 9. Spectral emission of $(Zn, Be)_2GeO_4$:Mn phosphors at −150 C (Mn/(Zn + Be) = 0.025 for all curves. Peak of all curves set equal to 100. Approximate relative heights of short wavelength peaks: 1 = 100; 2 = 140; 3 = 65; 4 = 80; 5 = 80; 6 = 45; 7 = 70).

Be/Zn 1: 0 2: 0.25 3: 0.43 4: 0.67 5: 1.0 6: 1.5 7: 2.3

The luminescence emission characteristics of $(Zn, Be)_2GeO_4$:Mn phosphors are, thus, seen to be qualitatively quite similar to those of the

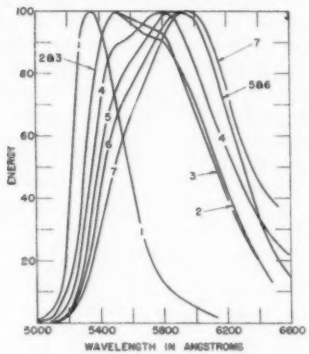

FIG. 10

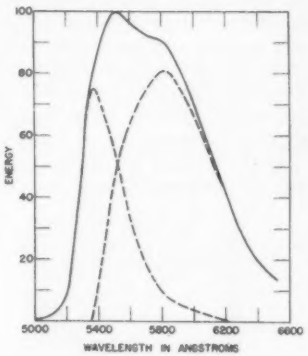

FIG. 11

FIG. 10. Spectral emission of $(Zn, Be)_2GeO_4$:Mn phosphors at −150 C (Mn/(Zn + Be) = 0.05 for all curves. Short wavelength peaks of all curves set equal to 100. Approximate relative heights of short wavelength peaks: 1 = 100; 2 = 55; 3 = 17; 4 = 10; 5 = 30; 6 = 45; 7 = 25).

Be/Zn 1: 0.0 2: 0.11 3: 0.25 4: 0.43 and 0.67 5: 1.0 6: 1.5 7: 2.3

FIG. 11. Resolution of the −150 C spectral emission of $(Zn_{0.8}Be_{0.2})GeO_4$:0.1 Mn into two bands.

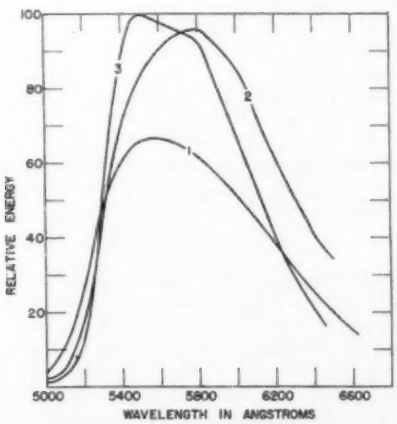

FIG. 12. Spectral emission of $(Zn_{0.8}Be_{0.4})GeO_4$:0.1 Mn at various temperatures 1. 25 C 2. −60 C 3. −150 C

$(Zn, Be)_2SiO_4$:Mn phosphors. One major difference between the two groups of luminescent compounds appears to be in the absence of any clear-cut "red" emission band in the high manganese bearing Zn_2GeO_4:Mn

phosphors at temperatures low enough to call forth this band in corresponding Zn_2SiO_4:Mn phosphors, or in $(Zn, Be)_2GeO_4$:Mn phosphors with very much less manganese. There is also a difference in the magnitude of the effect of beryllium and manganese in the two groups of phosphors. Larger amounts of both constituents are required in the germanates to cause much change from the emission of Zn_2GeO_4:Mn than are needed in the case of the silicates; in the latter phosphors, practically complete suppression of the green band is accomplished at room temperature, with the maintenance of a high luminescence efficiency in the red band, at a mole ratio of Be/Zn as low as 0.25 and a ratio of Mn/(Zn + Be) of as little as 0.066 (2).

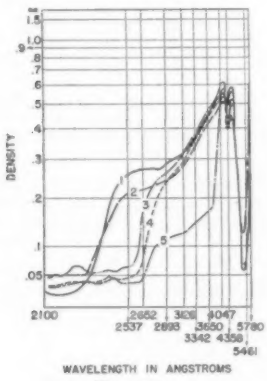

FIG. 13

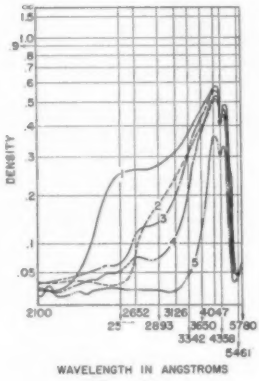

FIG. 14

FIG. 13. Reflection spectra of $(Zn, Be)_2GeO_4$ powders

1. $MgCO_3$
2. Be_2GeO_4
3. $(Zn, Be)_2GeO_4$, Be/Zn = 1
4. $(Zn, Be)_2GeO_4$, Be/Zn = 0.25–0.11
5. Zn_2GeO_4

FIG. 14. Reflection spectra of $(Zn, Be)_2GeO_4$:Mn powders

1. $MgCO_3$
2. $Zn_{1.6}Be_{0.4}GeO_4$:0.0 Mn
3. $Zn_{1.6}Be_{0.4}GeO_4$:0.01 Mn
4. $Zn_{1.6}Be_{0.4}GeO_4$:0.05 Mn
5. $Zn_{1.6}Be_{0.4}GeO_4$:0.18 Mn

ABSORPTION SPECTRA

The $(Zn, Be)_2GeO_4$:Mn phosphors were prepared in the usual powder form, hence good absorption measurements were not obtainable. A limited amount of data on the absorption characteristics as a function of composition was obtained, however, by a study of the reflection of these phosphors. For this purpose, phosphor plaques were irradiated by a Beckman hydrogen lamp, and the reflected light photographed with a Gaertner L250–93 quartz spectrograph. A plaque of $MgCO_3$ was used as a reference standard. Densitometer curves were prepared from the spectrograms using a Leeds & Northrup Knorr-Albers microphotometer. Tracings of these curves, with the small oscillations averaged out, are reproduced in Fig. 13–15.

The position of the absorption edge in the various phosphors can be found only approximately from these measurements, the uncertainty

being perhaps as high as ± 200 Å. From Fig. 13, it is seen that the edge for Zn_2GeO_4 is at about 2650 Å, with a considerable long-wave extension of the edge throughout the near ultraviolet. The introduction of beryllium appears to make no change in the position of the Zn_2GeO_4 edge, but the long-wave extension is considerably reduced.

The effect of manganese on the reflection spectra of $(Zn_{1.6}Be_{0.4})GeO_4$ phosphors is shown in Fig. 14. With increase of manganese concentration, the long wavelength extension of the edge absorption increases, until with sufficient manganese ($\frac{Mn}{Zn + Be} \geq 0.1$) a new edge is found at about 3400–3500 Å. The same effect is observed in beryllium-free Zn_2GeO_4 phosphors, as shown in Fig. 15.

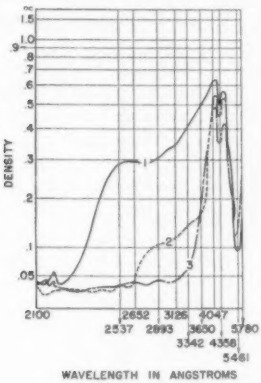

FIG. 15

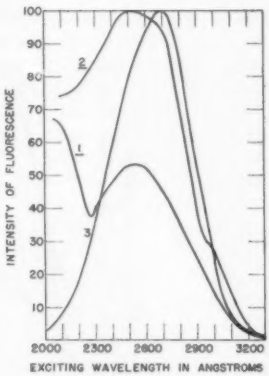

FIG. 16

FIG. 15. Reflection spectra of Zn_2GeO_4:Mn powders
1. $MgCO_3$ 2. Zn_2GeO_4 3. Zn_2GeO_4:0.18 Mn

FIG. 16. "Excitation spectra" of Zn_2SiO_4:Mn
1. Kroeger, Mn/Zn = 0.01 3. Present paper, Mn/Zn = 0.061
2. Kroeger, Mn/Zn = 0.053

EXCITATION SPECTRA

Excitation spectra of the phosphors were obtained using the system described in a previous paper (11), the excitation source consisting of a Beckman hydrogen lamp and Beckman monochromator. The phosphor was viewed by a 931A multiplier phototube provided with a Corning #3486 filter, the output of the phototube being amplified and recorded on a Brown recorder. As in our previous work, the intensity of the exciting light was not measured, hence the curves in Fig. 16 and 17 represent phototube response *vs.* wavelength of exciting light rather than a true excitation spectrum. Where sharp excitation bands exist, as in $CaCO_3$: (Pb, Tl, or Ce, + Mn), the data obtained by this method represent the excitation spectrum quite well, even if correction is not made for the vari-

ation of incident light intensity with wavelength. This is true because the output of the hydrogen lamp and the transmission of the monochromator both vary continuously, and not too rapidly, with wavelength. However, in the case of the Zn_2GeO_4:Mn and $(Zn, Be)_2GeO_4$:Mn phosphors reported here, the excitation bands are not sharp, and the curves represent a somewhat distorted excitation spectrum. The excitation curve for willemite, Zn_2SiO_4:Mn, obtained in our work is compared in Fig. 16 with the excitation spectrum for the same substance found by Kroeger (10). Kroeger's results were obtained by a method that differed from ours in several respects, and are apparently likewise uncorrected for the variation in incident exciting energy with wavelength.

The response curves for Zn_2GeO_4:Mn as a function of the manganese concentration are given in Fig. 17. With very low manganese concentrations, only one excitation band is observed. The maximum in the response

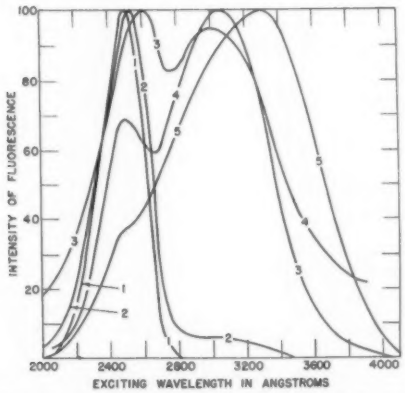

FIG. 17. "Excitation spectra" of Zn_2GeO_4:Mn
1. Mn/Zn = 0.00025 3. Mn/Zn = 0.0025 5. Mn/Zn = 0.088
2. Mn/Zn = 0.0005 4. Mn/Zn = 0.025

curve lies at about 2500 Å. The amount of ultraviolet radiation transmitted by the system dies off rather rapidly from 2500–2000 Å; therefore, the occurrence of an excitation "peak" at 2500 Å is not significant. The significant result is that the long-wave limit of this excitation band lies at 2700–2750 Å. Since the absorption edge of Zn_2GeO_4 itself was found to be at about this wavelength, this excitation band appears to arise from absorption in the host crystal.

As the manganese concentration increases, a new excitation band appears at longer wavelengths, and increases in intensity with respect to the 2500 Å band. The apparent peak of this longer wavelength excitation band is in the neighborhood of 3000–3300 Å, although again the position of the "peak" is not significant. The long wavelength limit of this second excitation peak lies at about 3900 Å, which agrees very roughly with the position of the absorption edge in zinc germanates with high manganese contents. The second excitation band is, therefore, connected with the

presence of the manganese activator in the crystal. With $(Zn, Be)_2GeO_4$:Mn, the situation is quite similar.

DISCUSSION

Of the measurements of luminescence emission, special interest attaches to the absence of any clearly defined "red" emission band in beryllium-free, high-manganese bearing Zn_2GeO_4:Mn at low temperatures, where the corresponding Zn_2SiO_4:Mn phosphors, and even low manganese content $(Zn, Be)_2GeO_4$:Mn, display such a band. It is, of course, possible that our inability to find evidence for such a band in the zinc germanates may be entirely a question of the resolution limits of our experimental arrangement, or that measurements at still lower temperatures might reveal its existence. We are inclined to believe that our resolution is adequate. Reference to curve 3, Fig. 9, will show that resolution of the emission of $(Zn_{1.4}Be_{0.6})GeO_4$:0.05 Mn into bands is already clearly evident at −150 C, while the existence of a second peak in the emission of $(Zn_{1.6}Be_{0.4})GeO_4$:0.05 Mn is just barely perceptible. Even if this barely resolved second peak in the latter curve is ignored, and the whole treated as a single band, the possible existence of another band is suggested here by the great broadening of the emission spectrum compared to that of the corresponding beryllium-free Zn_2GeO_4:0.05 Mn. The half-maximum width of the Zn_2GeO_4:0.05 Mn phosphor is about 320 Å; while the half-maximum width of $(Zn_{1.6}Be_{0.4})GeO_4$:0.05 Mn is about 570 Å, an increase of almost 80 per cent. In contrast to this, the broadening of the Zn_2GeO_4:Mn "green" emission band with increase in manganese concentration is very much less, a two hundredfold increase in Mn/Zn ratio increasing the half-maximum width by about 25 per cent, from 330 Å to 410 Å (cf. Fig. 4).

In both Zn_2GeO_4:Mn and Zn_2SiO_4:Mn, there is a distinct shift of the whole emission spectrum toward longer wavelengths with increasing manganese concentration. With Zn_2SiO_4:Mn, of course, there appears, in addition, a new band on the red side of the original band. We believe that the shift of the Zn_2SiO_4:Mn curve as a whole toward longer wavelengths cannot be the result of the growth of this new band, since the shift is quite marked, even at comparatively low manganese concentrations (cf. Fig. 5) where the "red" band has hardly appeared. The same holds true for Zn_2GeO_4:Mn (cf. Fig. 4) where the existence of a separate "red" band is apparently not involved. The reason for this spectral shift is not clear, but it may be related to the variation of lattice constant with manganese concentration; or alternatively, it may be that the increase in the number of "aggregated" Mn^{+2} -ions with increase of manganese concentration, instead of being responsible for the "red" band, is the cause of the shift and broadening of the "green" band.

Mn^{+2} -ion pairs, triplets, etc., must exist in Zn_2GeO_4:Mn to the same degree as in the isostructural Zn_2SiO_4:Mn of the same manganese content, and such aggregates can reasonably be expected to have about the same properties in both crystal hosts. In view of this, our results appear to conflict with the hypothesis assigning the "red" emission band to such "aggregate" centers.

It is interesting, however, that a consideration of the emission of Zn_2SiO_4:Mn alone reveals a rough quantitative relationship between the relative intensity of the "green" and "red" bands and the relative numbers

of "singlet" and "doublet" manganous ions. According to the description of the willemite and phenacite structures (5), the environment of a given M^{+2} -ion (Zn^{+2}, Be^{+2}—or Mn^{+2} substituting for Zn^{+2} or Be^{+2}) is as shown schematically in the accompanying Fig. 18. Each M^{+2} -ion, therefore, has four nearest M^{+2} -ion neighbors, if only M^{+2} -ions joined the same oxygen are considered nearest neighbors. On this basis, the number of aggregated Mn^{+2} ions can be calculated from probability considerations as a function of the Mn^{+2} concentration in the crystal, assuming a random entry of Mn^{+2} into Zn_2SiO_4, entirely by a $Mn^{+2} \rightarrow Zn^{+2}$ substitution. The results of such calculations (17) are shown in Table II.

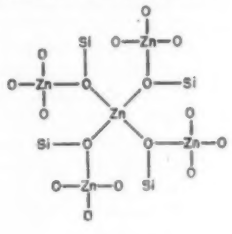

FIG. 18

TABLE II. *Probability of a Mn^{+2}-ion having x other Mn^{+2}-ions in nearest cation neighbor position where x is*

$(Mn^{+2})/(Zn^{+2})$	0	1	2	3	4	At least 1
0.001	0.996	0.004	$0.6\ (10^{-6})$	$4\ (10^{-9})$	$\sim (10^{-12})$	0.004
0.0025	0.990	0.01	$0.38\ (10^{-4})$	$6\ (10)$	$3.9\ (10^{-11})$	0.01
0.02	0.93	0.075	0.0022	$3\ (10^{-5})$	$1.5\ (10^{-8})$	0.07
0.05	0 83	0.17	0.012	$4\ (10^{-4})$	$\sim 5\ (10^{-6})$	0.17
0.1	0.68	0.27	0.041	0.0027	$\sim 7\ (10^{-5})$	0.32
0.2	0.48	0.38	0.116	0.015	$\sim 8\ (10^{-4})$	0.52
0.3	0.35	0.42	0.189	0.036	0.0028	0.65
0.4	0.26	0.42	0.25	0.067	0.0067	0.74
0.5	0.20	0.39	0.30	0.099	0.012	0.80
1	0.063	0.25	0.38	0.25	0.063	0.94

The ratio of the number of "green" band quanta (N_g) to the number of "red" band quanta (N_r) emitted by any phosphor should then be given by

$$\frac{N_g}{N_r} = \frac{P_1 f_g}{P_2 f_r}$$

where P_1 = probability of any given Mn^{+2} having no other Mn^{+2} in nearest neighbor positions

P_2 = probability of any given Mn^{+2} having one nearest Mn^{+2} neighbor

f_g = fraction of singlet Mn^{+2} -ions which are effective (green) luminescence centers.

f_r = fraction of "paired" groups which are effective (red) luminescent centers.

The factors "f" include the possibilities that only specially situated singlet or doublet Mn^{+2} ions may be effective emitters; that very likely only one ion at a time in doublets is an active center at any given moment; and that there may be a difference in the lifetime of the excited states of Mn^{+2} singlets *vs.* Mn^{+2} doublets. If the emission spectra of several high manganese content zinc silicates are replotted as the number of quanta emitted *vs.* wavelength, and the curves are then each resolved into two bands, one similar to the "green" band and the other to the "red" band, the ratio of areas under each sub-band then gives the ratio $\frac{N_g}{N_r}$. For phosphors of not too different manganese content, both f_g and f_r, and hence their ratio, should be approximately constant. This is found to be the case, as shown in Table III.

Although the above results are interesting, we do not attach great significance to them, in view of the observed difference between Zn_2SiO_4:Mn and Zn_2GeO_4:Mn. Furthermore, at the low temperatures in question, aggregates greater than pairs should also be expected to play some part in the luminescence, since here even pure manganese salts luminesce (12)[3]; and the agreement is very poor if one includes triplets, quadruplets, etc., in the calculations.

TABLE III

(Mn/Zn)	P_1	P_2	N_g/N_r	f_g/f_r
0.2	0.48	0.39	3	2.4
0.3	0.35	0.42	2.3	2.8
0.5	0.20	0.40	1.5	3

There is another observation which is not easily explicable on the basis of the "aggregate" hypothesis or on any hypothesis which restricts the role of beryllium solely to that of substitution for zinc, and which requires that such a substitution take place if the beryllium is to have any effect at all. This is the observation that beryllium concentrations exceeding the solubility of Be_2GeO_4 in Zn_2GeO_4 (and of Be_2SiO_4 in Zn_2SiO_4) have a decided effect on the luminescence spectrum. This cannot be explained on the basis of luminescence of Be_2GeO_4:Mn which may remain as a separate phase in these high-beryllia preparations, since samples of this material show no luminescence at room temperature. The existence of beryllium-rich solid solutions on the high-beryllium side of the Zn_2GeO_4-Be_2GeO_4 and Zn_2SiO_4-Be_2SiO_4 systems could alternatively be postulated. The further increase in prominence of the "red" band with increase in beryllium content of the formulation could then be ascribed to this second solid-solution phase, assuming it dissolved manganese to give a red-emitting phosphor. These assumptions would explain the effect of excess beryllium without recourse to either the coordination or the aggregate hypotheses. The effect of beryllium in promoting the appearance of the red band is evident, however, even when one works in a region of complete miscibility in the high zinc side of the Zn_2GeO_4-Be_2GeO_4-Mn_2GeO_4 and

[3] Reference 10, p. 19, curve 3. Fluorescence is observed in pure $MnSiO_3$ at −180 C, where all the nearest cation neighbors of any given Mn^{+2}-ion are also Mn^{+2}-ions.

Zn_2SiO_4-Be_2SiO_4-Mn_2SiO_4 systems. The emission spectrum varies regularly with increase of beryllium content within and beyond the solubility limit of beryllium. It, therefore, seems unwarranted to postulate the existence of another luminescent phase, having exactly the emission characteristics of the "red" band found in high-zinc bearing $(Zn, Be)_2GeO_4$:Mn, in order to explain the continued modification of the emission spectrum by beryllium contents lying beyond the solubility limit.

This apparently anomalous effect of excess beryllium is understandable from the replacement scheme based on the coordination hypothesis, for it should be noted that determinations of solubility of Be_2GeO_4 (or SiO_4) in Zn_2GeO_4 (or SiO_4) by x-ray diffraction studies, based, as they have been, solely on the observation of lattice constant changes, give information only with respect to the $Be^{+2} \rightarrow Zn^{+2}$ substitution. This does not preclude the simultaneous entry of Be^{+2} into the crystal in other ways which would produce no such large variation in lattice constant. The $Be^{+2} \rightarrow Si^{+4}$ and $Be^{+2} \rightarrow Ge^{+4}$ replacements that have been proposed would have much less effect on the lattice dimension than a $Be^{+2} \rightarrow Zn^{+2}$ substitution (cf. radii of Be^{+2}, Zn^{+2}, Si^{+4}, Ge^{+4}), and could continue to take place after the supposed limit of solubility of Be^{+2}—as determined by x-ray means—had been exceeded.

While the formation of near-neighbor pairs and larger activator clusters is certainly of highest importance in the analysis of luminescence phenomena, it appears to us that the origin of the red band in Zn_2SiO_4:Mn, $(Zn, Be)_2SiO_4$:Mn, $(Zn, Be)_2GeO_4$:Mn, and in other manganese-activated silicates is better accounted for in terms of coordination number of the manganese than in terms of the aggregation hypothesis. Thus the luminescence of Mg_2SiO_4:Mn is red even at very low manganese concentrations where aggregate formation is negligible. The most obvious difference between this compound and Zn_2SiO_4 is the coordination of the cation, the difference in symmetry and structure being a geometrical consequence of the difference in coordination. Both crystals are built up of SiO_4 groups isolated from each other by oxygen polyhedra containing the cation at their centers. In the case of the Mg_2SiO_4, the six oxygens are grouped octahedrally around the Mg (5), while in Zn_2SiO_4 the four coordinating oxygens form tetrahedra around the Zn^{+2} (or around the substituting Mn^{+2}). On the other hand, the variation in spectral emission of Mg_2SiO_4 with manganese concentration observed by Fonda and Froelich (7) has already been mentioned and must be accounted for. Here two emission bands are found; the first, visible at the lowest manganese concentrations, peaking at 6600 Å; the second, arising at higher manganese concentrations, having a peak at 7400 Å. Since the coordination hypothesis calls for only one red emission band in this phosphor, it appears reasonable here to look for an explanation of the 7400 Å band in the formation of Mn^{+2} -ion near neighbors as suggested by Maurer (6). Thus, though the strict coordination picture may require modification and refinement, it nevertheless is quite useful in explaining major differences in the spectral emission properties of a number of different manganese-activated phosphors.

It is of interest to compare absorption and excitation characteristics of $(Zn, Be)_2GeO_4$:Mn phosphors with those of the $(Zn, Be)_2SiO_4$:Mn phos-

phors. For Zn_2SiO_4, Kroeger (10) finds an absorption edge at 2250 Å. On the basis that (*a*) the (SiO_4) ion can be treated as a sphere of radius $2A$; (*b*) the Madelung constant (A_m) for $A^{II}\ B^{I}_2$ compounds is about 5 irrespective of structure type, hence A_m for Zn_2SiO_4 is 20; (*c*) polarization and the variation of repulsive forces accompanying electronic transfer from one ion to another are neglected, he calculates the position of the edge to be expected if the absorption act corresponds to each of the following transitions:

$$Zn^{+2} + SiO_4^{-4} + h\nu_a \rightarrow Zn^{+3} + SiO_4^{-5} \qquad (I)$$

$$Zn^{+2} + SiO_4^{-4} + h\nu_b \rightarrow Zn^{+1} + SiO_4^{-3} \text{ (separated from each other by large distances)} \qquad (II)$$

$$Zn^{+2} + SiO_4^{-4} + h\nu_c \rightarrow Zn^{+1} + SiO_4^{-3} \text{ (adjacent to each other)} \qquad (III)$$

The calculated values of the required energy are as follows:

$$E_A = 21 \text{ ev}; E_B = 8.1 \text{ ev}; E_C = 3.3 \text{ ev}$$

The observed edge being at about 5.5 electron volts (ev), Kroeger chooses mechanism (II) as the most probable absorption process. This interpretation is supported by his study of the variation of the position of the absorption edge in solid solutions of (Zn, Be)$_2SiO_4$ and (Zn, Cd)$_2SiO_4$. In the case of (Zn, Mn)$_2SiO_4$, however, the experimental results are not in agreement with this interpretation; mechanism (II) calling for the absorption edge of Zn_2SiO_4:Mn to be 2.2 ev to the short wavelength side of the Zn_2SiO_4 edge, while the observed shift is 1.4 ev to the long wavelength side. Kroeger points out that this discrepancy may be due to the neglect of the repulsive energy in the calculations. He, therefore, retains mechanism (II) as the interpretation of the absorption act in the Mn^{+2}-produced long-wave extension of the Zn_2SiO_4 edge, i.e.,

$$Mn^{+2} + SiO_4^{-4} + h\nu^{-4} \rightarrow Mn^{+1} + SiO_4^{-3} \text{ (separated from each other by large distances)} \qquad (II')$$

The lattice constant of Zn_2GeO_4 is about two per cent greater than that of Zn_2SiO_4, according to our measurements. Using the same simplifying assumptions with Zn_2GeO_4 that Kroeger has applied to Zn_2SiO_4, the coulomb energy term for the former is found to differ by about 1 ev from that of the latter crystal. The absorption edge in Zn_2GeO_4 is found experimentally to lie at the long wavelength side of the Zn_2SiO_4 edge, and the observed difference agrees quite well with the value calculated on the basis of mechanism (II). [Zn_2SiO_4 edge (Kroeger) at 2250 = 5.5 ev; Zn_2GeO_4 edge at 2650–2750 = 4.6 ev; difference = 1.1 ev.]

With the germanate, as well as with the silicate, absorption mechanism (II) predicts the wrong position of the "manganese" absorption edge with respect to the "zinc" edge. If again the position of the manganese edge in Zn_2GeO_4:Mn and Zn_2SiO_4:Mn is compared, the shift of this edge is in the right direction and of approximately the predicted amount. The lattice constant of Zn_2GeO_4:Mn is about 1.8 per cent greater than that of Zn_2SiO_4:Mn; hence the position of the manganese edge in the former crystal should be about 0.9 ev less than in the silicate. Taking Kroeger's (10) figure of 3000 Å (4.1 ev) for the position of the manganese edge in the silicate, and our value of about 3400 Å (3.6 ev) for the position

of this edge in the germanate, the result agrees only qualitatively with the predicted value of the difference. If we take as the Zn_2SiO_4:Mn and Zn_2GeO_4:Mn edges the long wavelength limits of their excitation spectra as found by us, the agreement is better. For Zn_2SiO_4:Mn the position of the edge from the above data is 3200 Å ($\sim$ 3.9 ev), while for Zn_2GeO_4 it is 3900–4000 Å ($\sim$ 3.2–3.1 ev), a difference of 0.7–0.8 ev. This makes plausible Kroeger's assumption that neglect of the repulsion term in his calculations on Zn_2SiO_4:Mn is the reason for the wrong sign and magnitude shift of the absorption edge in this phosphor compared to pure Zn_2SiO_4. Since the germanate is so similar to the silicate, chemically and structurally, one might expect that the error introduced by neglecting the repulsion term would be about the same in both cases, and should cancel out when the difference is taken. Our results on excitation and absorption indicate, then, a mechanism for these processes in Zn_2GeO_4 phosphors similar to that accepted by Kroeger for the Zn_2SiO_4 phosphors. In the case of the germanates, the edge of the fundamental lattice absorption band is at 2650 Å and absorption in this band leads to an electron transfer from GeO_4^{-4} to Zn^{+2}. The longer wavelength absorption and excitation is due to a similar electron transfer from GeO_4^{-4} to Mn^{+2}.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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INFLUENCE OF FLUXES ON THE CATHODOLUMINESCENCE OF ZINC SULFIDE PHOSPHORS[1]

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ABSTRACT

The relative cathodoluminescent efficiencies of silver-activated zinc sulfides and silver-activated zinc-cadmium sulfides fired with different fluxes have been determined.

Further evidence and arguments are advanced to substantiate a hypothesis first proposed by Gugel concerning the mechanism of flux action.

INTRODUCTION

Major factors which influence the luminescent characteristics of all inorganic phosphors are: (*a*) base matrix, (*b*) the kind and concentration of activators, (*c*) firing temperature, (*d*) atmospheric environment, and (*e*) flux or fluxes. While the effects of these factors on the photoluminescent characteristics of phosphors have been investigated more or less extensively, comparatively little information is available on their effect on cathodoluminescence. Since no positive correlations have yet been determined between cathodoluminescence and photoluminescence, the results of Lenard, Guntz, Rothschild, Kroeger, and others on photoluminescence, while serving as excellent guides to investigations on cathodoluminescence, do not give specific information. Such specific information was required in the development of the silver activated zinc and zinc-cadmium sulfides in use in the present television kinescopes.

To fulfill this need a program was instituted to determine the effect of factors (*d*) and (*e*) above on the cathodoluminescence of these materials. The variations due to factor (*d*) have already been published (1). This paper is concerned with factor (*e*).

Leverenz (2) has published fragmentary information directly bearing on this subject. Rothschild's (3) paper concerning the effect of the variations in the preparative conditions on the photoluminescence of zinc sulfide type phosphors served as a considerable stimulus to this work. Kroeger's (4) paper appeared, unfortunately, at the time our program was completed. His results would undoubtedly have influenced our experimental work. Our approach to the problem was slightly different than that of either Kroeger or Rothschild. Both were interested primarily in an explanation of the nature of the activator center. We, on the other hand, were more concerned with the differences observed by the use of the various fluxes, and sought, within the framework of other investigators, what the chemical nature of the flux might be. Of particular interest was the use of ammonium chloride, which, because of its ease of sublimation, would appear to have left the sphere of action before it could be effective.

[1] Manuscript received January 31, 1949.

EXPERIMENTAL

Materials.—RCA "luminescence pure" zinc sulfide and zinc-cadmium sulfide were used. These materials were prepared, with modifications, according to Einig (5). The sulfides were spectroscopically free of "heavy metals"; concentration of copper was less than 10^{-3} grams per gram, as evidenced by the fact that no green band was observed when the zinc sulfide:silver phosphor was irradiated with ultraviolet at elevated temperatures. Chemical analyses of a typical zinc sulfide preparation showed that the material was sodium- and chloride-free, but contained 0.3 per cent $ZnSO_4$, 0.2 per cent "H_2SO_4," and 1.1 per cent H_2O.

Chemically pure or reagent-grade commercially available fluxes were chosen in which the total heavy metal impurity content of each was 0.0005 per cent or less. To test whether this limit was sufficient, the sodium, barium, and ammonium chlorides were further purified as follows: The chemically pure materials were dissolved in hot water and then made slightly alkaline by the addition of a few drops of ammonium hydroxide. Hydrogen sulfide was passed through the hot solutions for $\frac{1}{2}$ to $\frac{3}{4}$ of an hour. The solutions were allowed to digest for several hours, after which they were filtered by suction through fritted glass funnels which were covered by layers of filter-paper pulp. The sodium and barium chlorides were precipitated fractionally by saturating their solutions with hydrogen chloride. The ammonium chloride was twice recrystallized by conventional evaporation-cooling techniques and then electrolyzed for six days with 0.2 ampere at 1.5 volts between platinum electrodes.

Table I shows that these purification procedures were without effect on peak or visual efficiencies (as defined below), since no detectable change between purified and unpurified fluxes was observed when tested with ZnS:0.015 per cent Ag fired at 1250 C. (Check samples were fired simultaneously.) On the basis of these results, it was deemed unnecessary to purify the remaining fluxes further, since it was apparent that no benefit could be gained.

Preparation of phosphors.—Aqueous solutions of known concentration of both activator and fluxes (bromides, chlorides, and iodides) were added in requisite amounts to the dry base material, which was then evaporated to dryness at 150 C. The mixture was ground and transferred to translucent silica-glass crucibles. In the case of the fluoride fluxes, the dry fluoride was added to the base, and the mixture was then ground thoroughly. In all cases the weight of the charge was approximately 50 grams.

A large silica-glass crucible served as a container for the several smaller silica-glass crucibles which contained the phosphor samples. The samples were fired in a furnace having automatic temperature control for $1\frac{1}{2}$ to 2 hours in order to reach the firing temperature of 1250 C for ZnS:Ag, or 1000 C for (ZnCd)S:Ag. The samples were kept at these temperatures for twenty minutes, after which they were removed and allowed to cool outside the furnace. During the firing process, the furnace atmosphere was kept slightly reducing to eliminate oxidation effects.

The phosphor block was inspected under ultraviolet light and all discolorations caused by crucible contamination were removed.[2] The de-

[2] It has since been found that little or no crucible contamination is encountered if transparent silica-glass containers are used and care is taken to remove the silicate

sirable center portion of the sample was washed first with an extremely dilute ammonium hydroxide-sodium sulfide solution, followed by three washings with distilled water, or until free from flux. Drying at 150 C for 8 to 24 hours completed the preparation.

Cathodoluminescent efficiencies and emission spectra were determined by using a defocused electron beam with a current density of 1.5 μ amp/cm^2, and an accelerating potential of 8000 volts. Peak efficiencies and spectral distribution of energy were measured by means of the spectroradiometer and the method described by A. E. Hardy (7); the visual efficiencies were determined with a Weston eye-corrected photocell. Peak efficiency is defined as the amount of energy at the wavelength of maximum emission relative to an arbitrary standard at its peak wavelength, expressed in relative units. Visual efficiency is the ratio of the brightness of the sample under test to that of an arbitrary standard as measured by an eye-corrected photocell, also in relative units.

TABLE I. *Effect of purification procedures on peak and visual efficiencies of fluxes tested with ZnS:0.015% Ag fired at 1250 C*

Flux	Visual efficiency (Relative units)		Peak efficiency (Relative units)	
	Purified	*cp*	*Purified*	*cp*
2% NaCl	100	101	100	99
2% $BaCl_2$	100	96	115	114
2% NaCl, 2% $BaCl_2$	104	96	108	111
4% NH_4Cl	89	101	104	109
4% NH_4Cl, 2% NaCl	108	108	109	110
4% NH_4Cl, 2% $BaCl_2$	88	84	99	99
4% NH_4Cl, 2% $BaCl_2$, 2% NaCl	105	107	91	95

RESULTS AND DISCUSSION

The variations in visual and peak efficiencies of various fluxes and flux combinations with ZnS:0.015 per cent Ag:1250 C, and (Zn(55)Cd)S:0.01 per cent Ag:1000 C, are shown in Tables I, II, III, and IV.

Table II shows the results obtained by adding specially purified NH_4Cl, NaCl, and $BaCl_2$, individually and in combination, to ZnS:0.015 per cent Ag:1250 C. The number of samples prepared is shown in the second column. Visual and peak efficiencies are averaged for the samples prepared. The average deviation is included to indicate the reproducibility of results.

Visual efficiencies are shown in Tables IIIa and IVa; peak efficiencies are shown in Tables IIIb and IVb. The values in both tables have been converted to relative values by arbitrarily assigning a value of 100 to the

layer after each firing. Translucent silica glass may be used without contaminating the sample if it is purified in anhydrous hydrogen chloride at 1000 C. Indications are that the red fluorescent layer, sometimes encountered with translucent silica glass, is attributable to iron (6), which diffuses from the silica into the sulfide. The iron is volatilized from the crucible surface by the reaction with hydrogen chloride at high temperature. Silicaware, so treated, may be used several times without discoloring of the sample.

samples fluxed with sodium chloride. Table IV presents a composite of values obtained from (Zn(55)Cd)S and (Zn(47)Cd)S. Several samples of

TABLE II. *Effect of flux variation (Na^+, Ba^{++}, NH_4^+, Cl^-) on peak and visual efficiencies of ZnS:0.015% Ag*

Flux†	No. of samples	Visual* efficiency (Relative units)	Peak* efficiency (Relative units)
NaCl	9	110 ± 7	123 ± 7
NaCl, $BaCl_2$	5	111 ± 6	120 ± 7
$BaCl_2$	3	103 ± 2	125 ± 10
NaCl, NH_4Cl	4	119 ± 3	130 ± 3
NH_4Cl	3	107 ± 8	124 ± 2
$BaCl_2$, NH_4Cl	2	91 ± 2	115 ± 0
$BaCl_2$, NH_4Cl, NaCl	2	113 ± 2	108 ± 2

* An arbitrary sample fluxed with sodium chloride (not of this series) was chosen as the standard. Figures preceded by ± are the average deviation.

† All fluxes used for this series received the special purification previously described.

TABLE IIIa. *Visual efficiencies in relative units of indicated fluxes tested in ZnS:0.015% Ag with 1.5 μamp at 8 kv*

Cation	Anion			
	F	Cl	Br	I
Li		145*		
Na		100	100	
K		89	88	100
NH_4	72	98	118	117
Mg		95		
Ca		118		
Sr	70	89		
Ba		93		

* Sample oxidized.

TABLE IIIb. *Peak efficiencies in relative units of indicated fluxes tested in ZnS:0.015% Ag with 1.5 μamp at 8 kv*

Cation	Anion			
	F	Cl	Br	I
Li	<50	75		
Na	<50	100	107	
K		74	101	82
NH_4	67	100	94	112
Mg		111		
Ca		112		
Sr	63	108		
Ba		102		

(Zn(55)Cd)S and (Zn(47)Cd)S were compared, and from this relationship, the (Zn(47)Cd)S values were converted to relative (Zn(55)Cd)S values, and averaged with the absolute values of the latter.

These results, when viewed in conjunction with other work recently published (2, 3, 4, 8, 9, 10, 11, 12, 13) clarify the action of fluxes to a greater extent than was previously possible. It is agreed by all investigators that fluxes affect efficiency and crystal growth of the phosphor, although the mechanism by which these results are effected is subject to some controversy.

Schlegel (9) has pointed out, as have others, that when chloride fluxes are used, zinc chloride can be detected in the first wash liquid. This observation can be easily confirmed by adding sulfide ion to one portion and silver ion to another; both will form *white* precipitates. The amount of this precipitate is quantitatively greatest when ammonium chloride is used

TABLE IVa. *Visual efficiencies in relative units of indicated fluxes tested in (ZnCd)S:0.01% Ag 55:45 with 1.5 μamp at 8 kv*

Cation	Anion			
	F	Cl	Br	I
Li	96	91		
Na	91	100	98	96
K		95	101	100
NH_4	110	90	86	100
Ca	82	93		
Sr	94	96		
Ba		99		

TABLE IVb. *Peak efficiencies in relative units of indicated fluxes tested in (ZnCd)S: 0.01% Ag 55:45 with 1.5 μamp at 8 kv*

Cation	Anion			
	F	Cl	Br	I
Li	102	84		
Na	91	100	104	98
K		87	103	100
NH_4	69	84	79	104
Ca	71	91		
Sr	100	90		
Ba		90		

as a flux. These results have led investigators (2, 8, 11, 12) to formulate the equations:

$$\dot{Z}nS + 2R'X \rightarrow ZnX_2 + R_2'S \quad \text{(I)}$$
$$ZnS + R''X_2 \rightarrow ZnX_2 + R''S \quad \text{(II)}$$

where $R' = NH_4^+$, Li^+, Na^+, or K^+; and $R'' = Ca^{++}$, Sr^{++}, Mg^{++}, or Ba^{++}; and $X = F^-$, Cl^-, Br^-, or I^-. Schlegel says, in effect, that these reactions are reversible, but his hypothesis from this finding is open to some question. Gugel's (12) hypothesis is much more plausible, since it takes into account the alkali or alkaline-earth sulfides formed. Gugel offers the explanation that, since the alkali and alkaline-earth chlorides are liquids

at the temperature of firing, solid solutions of these sulfides with zinc sulfide may occur. The following reasons are offered to lend additional support to this hypothesis:

1. If solid solution did not occur, then upon the addition of water in the first wash, both the zinc chloride and alkali sulfide would dissolve and react to form the original ingredients, zinc sulfide and alkali chloride. Too, zinc chloride is quite volatile at the temperature of firing, so that if there were excess of any constituent, the excess would be that of alkali sulfide. Since only zinc chloride was detected experimentally, it must be concluded that the sodium sulfide has entered into combination with the zinc sulfide. This amount need not be large; "activator concentration" less than 0.1 per cent may suffice.

2. Randall (10) has observed that no matter how thoroughly and carefully a product fluxed with sodium chloride is washed, sodium can always be detected spectroscopically.

3. It was noted qualitatively during this investigation that the spectral emission changes slightly when different fluxes are used. The flux could alter emission only if it became an integral part of the host lattice. Rothschild (13) and Gugel (12) have observed that the spectral emission of ZnS:Cu phosphorescence is altered by the use of different fluxing agents. The results reported by Gugel concerning the use of $MgCl_2$ as a flux are in doubt, because he does not mention whether the addition of $MgCl_2$ was effected through dry grinding of the anhydrous salt or of the hydrate, or whether it was added as a solution. If the addition was made by adding a solution or by dry grinding of the hydrate, some of the spectral shift could be caused by the incorporation of oxide ion formed in the decomposition reaction:

$$MgCl_2 \cdot 6H_2O \rightarrow MgO + 2HCl + 5H_2O \qquad \text{(III)}$$

The results obtained by Gugel with simultaneous use of Na_2S and $MgCl_2$ indicate that a hydrated form was used, since sodium sulfide can remove oxide ion.

4. It is difficult to see why, if fluxes act merely as solvents, changes in efficiencies occur with different halide fluxes. It is significant, too, as Schlegel has pointed out, that sulfates are not "fluxes," although they are liquids at the firing temperature. The results of this investigation show definitely that alkaline-earth chlorides give higher peak efficiencies in silver activated zinc sulfide than do alkali chlorides. Crystal size is not a factor, nor is the degree of crystallinity, since crystals of varying size can be obtained with sodium chloride as a flux by varying the firing time alone. The relative ratio of peak efficiencies to visual efficiencies remains unaltered by this variation. Large crystals of zinc sulfide can be grown by merely firing in hydrogen or ammonia, but in neither case are efficient phosphors obtained.

5. Rothschild (14) and Zhirov (15) claim that zinc and cadmium sulfides are soluble, in at least small percentages, in alkaline-earth sulfides. It is probable that the converse is also true.

6. Schleede (16) has shown, in an investigation of the blackening processes of zinc sulfide, that reaction between base and flux occurred; that is, zinc chloride could definitely be detected.

Accordingly, a considerable amount of circumstantial evidence indicates that a certain amount of flux, or the products of metathesis between flux and sulfide, may enter and become an integral part of the host lattice. Kroeger (17) has succeeded in proving experimentally that chloride ion remains as part of the host crystal. Strange (18) arrived at the same conclusion from the fact that only fluxed samples yield efficient phosphors, although the author feels that this fact alone is insufficient evidence.

Randall (11) has approached the flux-particle growth problem, not from the point of view of the flux as a solvent, but from the apparent role of the flux as inhibitor of sublimation. He performed experiments which show that when cubic zinc sulfide is sublimed below the transition temperature of 1020 C, the sublimate is obtained in the metastable wurtzite form. In the presence of a flux, no wurtzite is formed below 1020 C. He explained this phenomenon by hypothesizing that the flux forms a protective coating about the zinc sulfide particles, and hence inhibits sublimation, i.e., the formation of wurtzite. Above the transition temperature, the fluxes assist in the crystallization of wurtzite; that is, the solvent action of the flux is then operative.

The efficiency of ammonium chloride in promoting crystal growth may be explained by a hypothesis based on reaction in the gas phase. At the firing temperature, ammonium chloride is completely dissociated into ammonia and hydrogen chloride. This investigation has established that either ammonia or hydrogen causes crystal growth of zinc sulfide; this growth can be explained only through a gas-phase reaction with the mechanism:

$$H_2\uparrow + ZnS\downarrow \rightarrow Zn\uparrow + H_2S\uparrow, \text{ followed by} \qquad (IV)$$
$$Zn\uparrow + H_2S\uparrow \rightarrow ZnS\downarrow + H_2\uparrow \qquad (V)$$

i.e., a strictly reversible process. Ammonia can react directly in the fashion

$$2NH_3 + 3ZnS \xrightarrow{heat} 3Zn\uparrow + 3H_2S\uparrow + N_2\uparrow (N_2H_4, ? \text{ etc.}) \qquad (VI)$$

followed by the reaction indicated by equation (V). Or, the ammonia might first dissociate

$$2NH_3 \xrightarrow{heat} N_2 + 3H_2 \qquad (VII)$$

with reactions of type (IV) and (V) following. This type of reaction may yield products different from those obtained by sublimation.

Leverenz (2) has shown that, when ammonium chloride is used as a flux, the emission is shifted toward the blue. Since the incorporation of oxide ions causes a shift toward the green, this property of ammonium chloride may be explained by its ability to remove these oxy-ions, either in solution or during firing. The mechanisms by which oxy-ions can be removed are varied:

(*a*) Removal of zinc oxide by ammonium chloride solution:

$$ZnO + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + H_2O \qquad (VIII)$$

$$Zn(NH_3)_2Cl_2 \xrightarrow[heat]{gentle} ZnCl_2 + 2NH_3 \qquad (IX)$$

(*b*) Removal of zinc sulfate by ammonium chloride solution:

$$2NH_4Cl + 2ZnSO_4 \rightarrow Zn(NH_4)_2(SO_4)_2 + ZnCl_2 \qquad (X)$$

(Upon evaporation the less soluble zinc-ammonium sulfate will crystallize first, while the zinc chloride will tend to remain in solution.)

(*c*) Removal of zinc oxide by firing with anhydrous ammonium chloride:

$$3ZnO + 2NH_3 \rightarrow 3\,Zn\uparrow + 3H_2O\uparrow + N_2\uparrow \qquad (XI)$$
$$ZnO + 2HCl \rightarrow H_2O\uparrow + ZnCl_2 \qquad (XII)$$

That equation (XI) predominates over a corresponding equation with zinc sulfide was shown by firing zinc sulfide samples containing measured additions of zinc oxide in hydrogen, ammonia, and purified nitrogen. The samples fired in nitrogen showed a shift toward green emission, which was linear in respect to amount of added oxide. Those fired in hydrogen or ammonia showed no shift toward the green at all, even when up to 3 per cent oxide had been added, which shows that all oxide had been effectively removed from the sphere of the activator center.

The zinc chloride, which was obtained in all cases as a by-product, has been shown by Leverenz (8) to be a moderately efficient flux. As has been mentioned previously, considerable amounts of zinc chloride (much greater than obtained by the use of any other chloride) were found in the wash liquid of the samples fluxed with ammonium chloride.

Ammonium chloride also causes much more rapid crystal growth than any other fluxing agent tested, probably as a result of the dual fluxing action occasioned by its decomposition products: gas-phase recrystallization due to ammonia (equations VII–IX) and solvent action of zinc (cadmium) chloride formed by the reaction

$$ZnS(CdS) + 2HCl \rightarrow ZnCl_2(CdCl_2) + H_2S \qquad (XIII)$$

This action can be verified by microscopic examination of particle sizes of samples fluxed by ammonium chloride and any other fluxing agent. It was verified visually when a zinc-cadmium sulfide fired with ammonium chloride was compared with the sample fired with sodium chloride. The washed product of the sample fluxed with sodium chloride showed a pale yellow reflected color; that with ammonium chloride was dark yellow. The change in reflected color was only a particle-size phenomenon; the sample fluxed with ammonium chloride had a particle size three to four times that of the sample fluxed with sodium chloride.

In the zinc-cadmium sulfide tests, spectral shifts resulting from the use of different fluxes were more pronounced than those observed when only zinc sulfide was used. This variation of spectral shift can be explained either by the selective reaction of the flux with one component, or by the greater ease of diffusibility of certain alkali or alkaline-earth sulfides into a particular structure.

Another lesser function of a halide flux might be to remove some of the "killers," such as iron or nickel as volatile chlorides.

It is of some interest that, in the zinc-cadmium sulfide series, all fluorides give narrow emission bands. We are thus led to the conclusion that the flux anion, at least in some cases, alters the spectral distribution. Whether

the anion enters through the medium of the original flux (e.g., NaF), or through the medium of a reaction product (ZnF_2), has not been experimentally determined.

It would appear that Gugel's hypothesis of solid solution should be expanded to include not only the alkali or alkaline-earth sulfides, but the original flux, or flux anion-base cation product.

If these hypotheses can be upheld by further experimentation, we could, in general terms, say that the action of the flux:

1. Increases crystal size through either (*a*) gas-phase recrystallization, (*b*) solvent action, or (*c*) both.
2. Affects spectral emission distriaution because either the flux or its reaction-products with the host material may form solid solutions with the host lattice.
3. Affects the efficiencies of the phosphor because these solid solutions are more conducive to formation of a crystal having Frenkel and/or Schottky defects, or lattice distortions. It appears that all phosphors are crystals under strain, although the strain may be impressed by any of several means.

This hypothesis is not weakened by the experimental fact that (ZnMn)S (18) and (ZnCd)S (19) phosphors show moderate efficiency when prepared without flux. In these cases, the lower free energy of the resultant solid solution at high temperature causes the reaction to proceed without the action of a flux. Crystal defects and distortion are occasioned in the same manner as those of a single component with a flux, since both are solid solutions.

Many workers have considered the flux to be responsible in some manner for the incorporation of the activator into the base lattice. There is no doubt that the flux facilitates the incorporation of the activator, since it causes recrystallization, during which the activator can be distributed throughout the lattice. The hypothesis that activator ions are too large to enter the lattice and, hence, must be reduced to the free element through some reaction of the flux is fallacious and untenable. That elemental copper can exist in a sulfide-surfeited atmosphere is quite unreasonable. Schlegel (9) contradicts himself on this point, saying that copper cannot diffuse except atomically, and yet pointing out that copper has a greater "affinity" for sulfur than has zinc. It is possible that there is a resonance phenomenon occurring, with copper at one instant being "atomic" and at another "ionic." Diffusion of solids into solids is not governed primarily by consideration of ion or molecule size. Even if copper sulfide cannot diffuse into zinc sulfide, there is no reason why zinc sulfide cannot diffuse into copper sulfide. The net result is copper activation by copper ions.

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NEW ZINC SULFIDE PHOSPHORS ACTIVATED BY PHOSPHORUS[1]

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ABSTRACT

The present paper describes a new series of ZnS phosphors in which the activator is the nonmetal phosphorus. This gives a range of unsaturated colors varying from pale blue to yellow as the phosphorus content is increased.

The physical and chemical characteristics, including methods of preparation, of the new phosphors are fully described.

INTRODUCTION

It is well known that blue fluorescing zinc sulfide can be obtained without the use of any specially added activator; it is generally accepted that the activating atoms are zinc atoms which are present in stoichiometric excess in the lattice. Other heavy metal activators in zinc sulfide, such as Ag, Cu, and Mn, give rise to blue, green, and yellow fluorescent colors, respectively, and these colors are modified by the addition of cadmium sulfide to the zinc sulfide. The effect of the cadmium sulfide is to cause the peak of the fluorescent band to move toward longer wavelengths.

Nonmetallic activators do not appear to have been used in sulfide phosphors. The present paper describes a new series of zinc sulfide phosphors in which the activator is the nonmetal phosphorus (1). This gives a range of fluorescent colors varying from blue to yellow as the phosphorus content is increased. The method of firing also markedly affects the color. Some of the intermediate colors have broad spectral emission bands when excited by long-wave ultraviolet radiation or cathode rays. Using these phosphors, good white television screens have been prepared without the use of the usual blend of blue and yellow fluorescing powders.

This property of the new phosphors may prove of considerable technical importance, since color separation is avoided during application of the screen. As a result, screens coated with these powders are very uniform, a feature which is particularly noticeable in a projected picture. The short yellow afterglow, which most of these powders exhibit, has not been found detrimental to picture quality. As far as experience goes, the single component white screen is less affected by processing than screens containing zinc cadmium sulfide. The single component also possesses obvious advantages over mixed powders for application by settling techniques.

The method of preparation of the new phosphors is fully described and an account is given of the variation of spectral emission with composition.

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PREPARATION

Zinc sulfide and fluxes.—The zinc sulfide is precipitated from highly purified solutions and thorough'y washed. Freedom from metallic impurities such as iron, cobalt, nickel, copper, etc., which inhibit the luminescence or produce a different activation of the zinc sulfide, is of the greatest importance. Added fluxes are not essential, but their use tends to improve the luminescent brightness of the product. A satisfactory flux comprises 10 per cent of magnesium chloride and 3 per cent of sodium chloride by weight of the zinc sulfide.

Source of phosphorus.—The phosphorus can be added to the raw zinc sulfide in a wide variety of forms which must be of high purity. Thus it can be added either as the element, red phosphorus, or as a compound such as a phosphide, e.g., Zn_3P_2, or a sulfide, e.g., P_2S_5. However, it can also be added as an oxy-salt of phosphorus such as a hypophosphite, phosphate, etc., of zinc, calcium, sodium, or ammonium.

The color of the luminescence excited by any given radiation depends on the amount of phosphorus introduced, the source of phosphorus used, and the firing conditions. The change in fluorescent color is always from the characteristic blue of "pure" crystalline zinc sulfide through intermediate

TABLE I. *Effect of increasing phosphorus content on color of fluorescence. Phosphorus added as* $(NH_4)_2HPO_4$. *Firing temperature 950 C*

Per cent by weight of phosphorus added before firing	Color of fluorescence
0	Blue
0.1	White
0.2	Yellow white
0.5	Bright yellow
1	Yellow
2	Deep yellow

white and yellow shades to a deep yellow or even dull orange color as the amount of phosphorus is increased. These effects are shown in Table I.

The intensity of the fluorescence becomes somewhat reduced when high concentrations of phosphorus are used and, in general, amounts less than 5 per cent by weight introduced before firing give the best results. Some loss of phosphorus during firing is inevitable and the amounts left in the finished powder are certainly less than the amounts added initially. Colorimetric methods of analysis indicate that a trace of phosphorus in the fired product is sufficient to produce a shift in color toward the yellow.

Firing conditions.—Firing is best carried out under reducing conditions. A slow stream of hydrogen gas provides a suitable atmosphere during the heat treatment but other reducing gases, such as carbon monoxide, are effective. Phosphorus present after the heat treatment in a higher state of oxidation, for example as a phosphate, acts merely as a diluent and, if colored, is additionally objectionable. It will be clear that the fluorescent color, which depends on the amount of "reduced" phosphorus present in the lattice, is strongly influenced by the effectiveness of the reducing atmosphere during firing.

Phosphorus compounds which decompose thermally with the evolution

of reducing gas, diammonium hydrogen phosphate, for example, may themselves be used to provide the reducing atmosphere during the preparation, provided the heating is carried out in a tightly plugged boat. It is, however, difficult to obtain consistent results by this method.

The temperature of the firing is more critical than in the preparation of normal zinc sulfide phosphors, since care must be taken to avoid undue loss of phosphorus during firing. The effect of too high a temperature or prolonged heating is to produce blue fluorescing phosphors. In view of the loss of phosphorus by volatilization, careful control during firing is necessary to insure repeatability of the product. Table II shows the effect of heating mixtures of zinc sulfide and 1 per cent by weight of ammonium phosphate for half-hour periods at various temperatures in hydrogen; it will be seen that phosphor formation only takes place above 600 C.

Many experiments have been carried out on the use of phosphorus alone or in conjunction with metal activators, such as copper and manganese, in zinc sulfides. Up to the present, no useful results have been obtained. If cadmium sulfide is present, it becomes reduced during firing with consequent discoloration of the powder.

TABLE II. *Effect of firing temperature and method of excitation on fluorescent brightness and color*

Temperature (C) of heating during preparation	Fluorescence under excitation by			
	3650 Å	2537 Å	Cathode rays (6000 v)	X-rays (45 kv)
600	None	None	—	—
700	Weak yellow	Very weak yellow	Weak white	Pale green blue
800	Weak yellow	Very weak yellow	Weak white	Pale green blue
900	Moderate yellow	Weak yellow	Yellow	Yellow white
1000	Bright yellow	Yellow	Bright white	Yellow white
1100	Bright blue-white	Blue	Bright deep blue	Deep blue

Excitation and emission characteristics.—As already mentioned, the phosphorus activated sulfides are excited by 3650 A radiation, x-rays, and cathode rays, and in this, as in all other respects except spectral emission, they closely resemble normal zinc sulfide phosphors.

The curves in Fig. 1 show the spectral energy distribution of the fluorescent light emitted under long-wave ultraviolet excitation. The behavior under cathode rays is similar. At very low concentrations of phosphorus, the normal blue band of zinc sulfide with its peak at about 4600 Å predominates (curve A). The effect of the phosphorus activator is to introduce a new band in the yellow with a peak close to 5600 Å. With added concentrations of phosphorus of the order of 0.5 per cent, the blue band is largely suppressed (curve E). By suitably arranging the conditions, any desired ratio of blue to yellow bands can be achieved. Thus with about 0.25 per cent of added phosphorus, both the blue and yellow bands are well developed and the resultant color of the emitted light is substantially white (curve D). The curves in Fig. 2 show that such a phosphor is similar in spectral energy distribution to the white sulfide mixture shown by Leverenz (2).

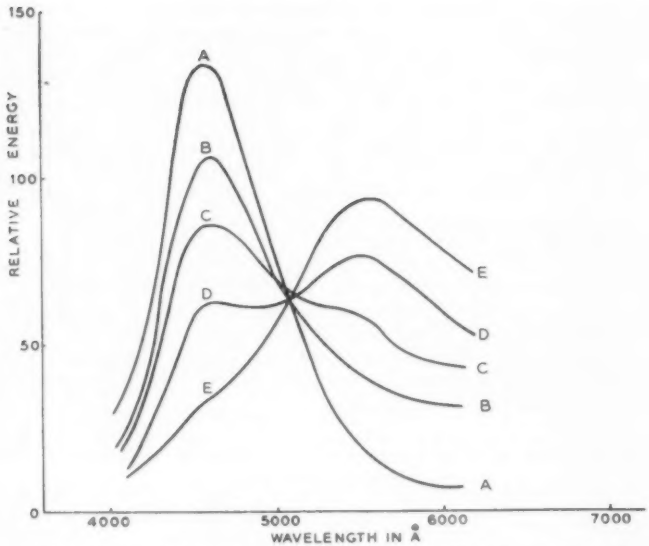

FIG. 1. Spectral energy curves with increasing phosphorus contents

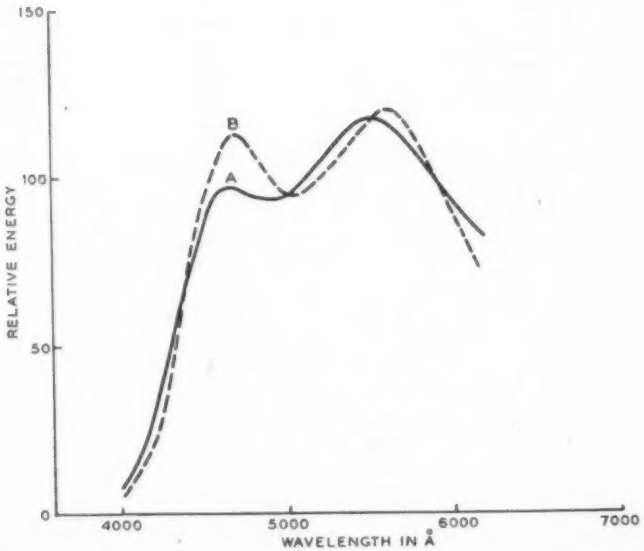

Fig. 2. Spectral energy curves of (A) phosphorus activated single component white sulfide, (B) three component sulfide mixture.

The curves in Fig. 2 are presented on the usual equal area basis. The phosphorus activated sulfides have given screen efficiencies some 30 per cent higher than conventional mixed sulfide screens prepared under similar conditions. This no doubt is largely due to the greater blue emission of the mixed powders which is clearly shown in Fig. 2.

The stability of the phosphors appears to be similar to that of the blue component of the conventional mixture and, therefore, greater than that of the cadmium-containing yellow component. Particle size can be varied in similar manner to normal sulfides. So far as the utilization of the phosphors is concerned, their phosphorescent behavior is similar to the usual sulfide materials.

Position of the activator in the lattice.—The curves in Fig. 1 suggest that phosphorus is behaving as a true activator rather than a lattice modifier, such as cadmium sulfide which, with increasing concentration, produces a progressive shift in the emission bands toward the red.

The position occupied by copper and silver atoms or ions in zinc sulfide phosphors is frequently assumed to be interstitial; evidence for this assumption is indirect and is based mainly on the ease with which these activators enter the lattice at low temperatures (300–400 C). In a recent paper, Kroeger and Hellingman (3) have shown the essential importance of the halogen ions (Cl^-, Br^-, and I^-) in the formation of the blue centers of ZnS(Ag), ZnS(Zn), and ZnS(Cu) phosphors. They assume that these centers are Ag^+Cl^- and Cu^+Cl^-, or the corresponding bromides or iodides.

The position occupied by manganese as activator in zinc sulfide has been clarified by x-ray examination, which shows that substitutional solid solutions are formed up to 52 molar per cent of manganous sulfide (4). It is interesting to note that phosphors activated by manganese require a relatively high temperature (*ca.* 800 C) for this substitution to take place. In the amount which can be added without causing discoloration, and in the temperature at which entry into the lattice occurs, manganese shows marked difference from copper and silver as an activator of zinc sulfide.

In both these respects, the new phosphors show a similarity to manganese activated zinc sulfide phosphors. Thus, the amount which can be added without discoloration is of the order of a few molar per cent of phosphorus, while the temperature needed for incorporation of the activator is about 700 C and upward. So far, x-ray examination of these compounds has not revealed any significant deviation in structure from the unactivated zinc sulfide phosphor. Substitution of negative phosphorus ions for sulfur ions in the lattice would, however, give only a slight lattice expansion due to their similarity in ionic radius. The possibility of interstitial entry into the lattice seems probable only if the phosphorus is present as a basic ion or in the atomic state.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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ELECTRON TRAPS AND INFRARED STIMULATION OF PHOSPHORS[1]

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ABSTRACT

Extensive studies have been made of the relation between electron trap distributions, as shown by thermoluminescence experiments, and the infrared stimulation characteristics of phosphors. A large number of conventional zinc and alkaline earth sulfide phosphors, as well as the special types of infrared sensitive phosphors, have been investigated. Experiments were made over a wide range of temperature from 77 to 600 K. The principal results of these experiments are summarized as follows:

1. There appears to be no direct relation between the stimulation spectrum of a phosphor and a particular group of electron traps. In general, during stimulation, electrons are ejected most readily from the shallowest electron traps present. The ability of the stimulating radiation to empty deeper traps increases as the wavelength of the radiation decreases. There are, however, two types of association between the stimulation spectrum bands and groups of electron traps. In certain phosphors, which usually have a complex stimulation spectrum, monochromatic irradiation in one part of this spectrum reduces preferentially this part of the spectrum, although it may affect the whole spectrum. Such irradiation appears, however, to have no selective effect in ejection of trapped electrons. The second kind of association is the following. In some phosphors certain groups of electron traps must be filled for a particular band in the stimulation spectrum to appear. However, when these traps are filled, they can be emptied by stimulation at shorter wavelengths.

2. Large differences are found between the light sums due to the release of trapped electrons by thermal and by optical activation. The light sum for stimulation is often much less than that for thermoluminescence in conventional phosphors, but very much the reverse is true of some infrared sensitive phosphors, as shown previously by other workers.

3. When phosphors are excited at a given temperature and then cooled in the dark, the stimulation spectrum obtained at the low temperature is similar to that observed at the excitation temperature, though reduced in intensity. The intensity decreases with temperature and, below a certain critical temperature, it is impossible to obtain stimulation in particular spectral bands. From these results, it is inferred that a thermal activation process is essential to stimulation; this is similar to the photoconductivity effects in alkali halides due to the optical ejection of electrons from F centers.

4. In previous studies at this laboratory, it was shown that, in the phosphorescence and thermoluminescence of sulfide and silicate phosphors, no retrapping of the released electrons takes place. However, when traps are emptied by infrared stimulation, a considerable degree of retrapping occurs. The theoretical implications of this effect are discussed.

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The above studies have furnished significant evidence on the stimulation process in phosphors, but they indicate no simple relation between the thermal and optical release of trapped electrons. It is hoped to clarify the position in this respect by making more precise measurements of stimulation, absorption, and thermoluminescence on single crystals of less complex luminescent solids.

INTRODUCTION

Since the development of sulfide phosphors whose luminescence can be stimulated by infrared radiation, there have been numerous investigations of their physical characteristics (1). These have been directed toward a better understanding of the basic physical processes involved. However, there are many significant experiments which have not been carried out on these phosphors, and very few observations of importance have been made on the stimulation of conventional sulfide phosphors.

In this paper, we describe studies made during the past year of different classes of sulfide phosphors, which have as their object the correlation of infrared stimulation characteristics with the phenomena of phosphorescence and thermoluminescence due to electron traps. Techniques of some precision have been developed in this laboratory for the study of electron trap distributions and the filling of electron traps under controlled conditions of excitation and temperature (2). In the following studies, we have used these techniques to determine how irradiation of phosphors by infrared radiation affects trapped electrons. By such investigations, we have found certain definite, though complex, relations between the stimulating radiation and the ejection of electrons from traps. For example, a significant difference between optical and thermal ejection of trapped electrons is the absence of retrapping of the electrons after thermal ejection (2), but its presence when traps are emptied by infrared radiation.

In reviewing past studies of infrared sensitive phosphors, we have found that the properties of most phosphors have been investigated thoroughly only at room temperature. Some qualitative observations on zinc sulfide phosphors at low temperatures have been made by Fonda (3). There has been a tendency to use phosphor pellets whose thickness introduces nonuniform excitation and irradiation conditions, an unnecessary complication in any experiment. The decay of the stimulated emission and light sums have been made, in most cases, using heterochromatic infrared radiation. In our experiments, we have used monochromatic radiation and our phosphor layers always have been very thin.

In order to investigate the release of stored energy by infrared radiation, we first verified relevant facts reported by previous workers. There is no doubt that infrared irradiation of phosphors, which produces either stimulation or quenching of luminescence, results in the emptying of electron traps. It has been shown also that there is no simple correlation between the wavelength of the radiation ejecting the trapped electrons and the trap depth distribution; the latter is determined by the thermal glow curve experiment (4, 5). Thus, the Franck-Condon principle does not apply to this case. It has been observed that the "light sums" obtained during thermoluminescence are rarely the same as those obtained by stimulation. Their ratio appears to depend on the particular phosphor, on

the excitation conditions, and on the phosphor temperature. We shall refer to the ratio of the *optical light sum* to the *thermal light sum* as the *light sum efficiency*. It is also known that at room temperature conventional phosphors, such as silver and copper activated zinc sulfides, show little or no stimulation by infrared radiation, but that their electron traps may be emptied by radiation of suitable wavelength. The light sum efficiency of these phosphors is always less than unity at room temperature.

The many phosphors which we have investigated may be grouped together as follows:

(a) Conventional zinc sulfide phosphors: ZnS-Zn, ZnS-Ag, ZnS-Cu.
(b) Infrared sensitive zinc sulfide phosphors: ZnS-Cu-Pb.
(c) Conventional alkaline earth sulfide phosphors: CaS-Bi, CaS-Pb.
(d) Infrared sensitive alkaline earth sulfide phosphors: SrS-Ce-Sm, SrS-Eu-Sm, SrSeS-Eu-Sm.

It is possible to describe experiments only on a few of the representative specimens in each group. The types of experiments we have made on each phosphor may be summarized as follows: (*a*) measurement of thermal glow curves after excitation at different temperatures and for given excitation and stimulation conditions; (*b*) measurements of stimulation spectra after excitation at a given temperature, and at various other temperatures after excitation at the given temperature; (*c*) measurement of thermal and optical light sums after excitation under known conditions at various temperatures; and (*d*) measurement of the decay of stimulated emission with time at various temperatures and for different irradiation wavelengths.

The chief objects of these experiments were as follows: (*a*) to find out whether any definite correlation exists between the trap distribution of a phosphor and its stimulation or quenching spectrum, for example, to determine whether longer wavelength infrared radiation affects only the shallower electron traps, since it has a smaller quantum energy; (*b*) to determine whether electrons ejected from traps by irradiation can be retrapped, a process which does not usually occur after thermal ejection of trapped electrons (2); and (*c*) to determine light sum efficiencies as a means of studying nonradiative dissipation of energy in phosphors.

EXPERIMENTAL TECHNIQUES

Following the usual method adopted in this laboratory, the phosphor specimen was always mounted in vacuo on a rhodium plated copper block forming part of a metal Dewar vessel. The block could be maintained at different temperatures, or its temperature varied at different rates over the range from 77 K to more than 600 K. Excitation of the phosphor was by a 125 watt high-pressure mercury arc in a quartz lamp, used with suitable filters. For zinc sulfide phosphors, 3650 Å radiation was selected, while for the alkaline earth sulfides, a wider band of radiation extending to 2537 Å was selected by a Corning 986 filter. The emission from the phosphor was focused onto the cathode of an R.C.A. 931A photomultiplier tube. Suitable Wratten filters were employed to select particular emission bands of phosphors. Other filters served to remove undesirable radiation, such as that scattered by the phosphor when irradiated. For infrared radiation, monochromatic radiation was provided

by a quartz monochromator with a tungsten lamp operated at about 2650 C as source. At 6500 Å, the half width of the monochromator beam was about 200 Å. In terms of quantum energy, which we use in our results as a better expression of the physical qualities of the radiation, this is a half width of about 0.06 electron volt (ev) over the range from 1 to 3 ev.

The output from the photomultiplier was amplified by a directly coupled amplifier with a low frequency response (band width a few cycles per second). The output of the amplifier was fed to the Y plates of a cathode ray tube. The X deflection was provided by one of two variable potentiometers connected to voltage sources (about 350 v, direct current). One potentiometer was geared to the wavelength drum of the monochromator, while the other was geared to a synchronous motor, which provided a slow linear sweep for decay and thermal glow measurements. The use of the first potentiometer enabled stimulation spectra to be displayed on the cathode ray tube screen, while the other potentiometer provided a means of displaying decay and thermal glow curves. Spectra and decay or glow curves were recorded by a camera focused onto the screen.

Since the stimulation spectra are obtained by irradiating the same layer of phosphor with different wavelengths in turn, it is essential to avoid spurious results arising from the enhancing of part of the stimulation spectrum by previous irradiation in another part. We found that the true spectrum was obtained by traversing the monochromator from long to short wavelengths. In some experiments involving the use of maximum sensitivity of the apparatus, the long time constant of the amplifier caused a "lag" effect in the spectra. This gave rise to a small shift in spectral maxima and is shown in some of our figures, as we shall indicate.

The stimulation spectra given in the next section are all corrected so that they represent the stimulated emission intensity for the same number of quanta of stimulating radiation at each wavelength. In this way, a more correct idea is given of the effectiveness of different wavelengths in producing stimulation than would be so if equal energy conventions are used. As stated above, we give a quantum energy scale for the spectra together with the wavelength scale. We shall describe particular experimental procedures where necessary in the presentation of results.

EXPERIMENTAL RESULTS

Conventional zinc sulfide phosphors

At ordinary temperatures, there is no marked stimulation of the emission of conventional zinc sulfide phosphors by infrared radiation, although such radiation may eject trapped electrons. However, at low temperatures, many of these phosphors show marked stimulation. The efficiency of stimulation, by which we mean the initial brightness for a given irradiation, is not very different for the various phosphors studied. This applies also to the copper-lead activated phosphors described later. The stimulation spectra are different for the different phosphors. In Fig. 1, we give spectra for different phosphors with different activating impurities after excitation at 90 K. In Fig. 2, we give the thermal glow curves for some of these specimens (warming rate for all glow curves in this paper is 3 K/sec). Some of these phosphors are now considered in detail.

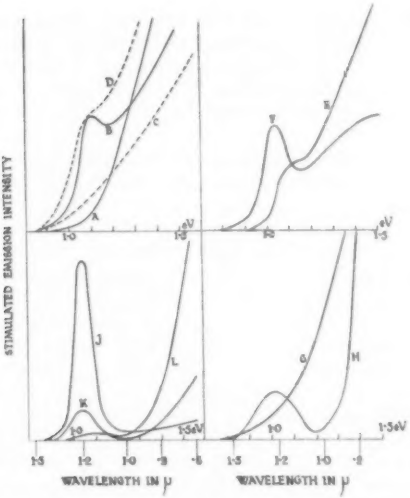

FIG. 1. Stimulation spectra of zinc sulfide phosphors at 90 K

A. ZnS-Zn
B. ZnS-Zn (trace Cu)
C. ZnS-Ag
D. ZnS-Ag (trace Cu)
E. ZnS-Zn (trace Cu) long to short wavelength traverse
F. ZnS-Zn (trace Cu) short to long wavelength traverse
G. ZnS-Mn (2%)
H. ZnS-Cu, specimen 1
J. ZnS-Cu, specimen 1
K. ZnS-Cu, specimen 2
L. ZnS-Cu, specimen 4

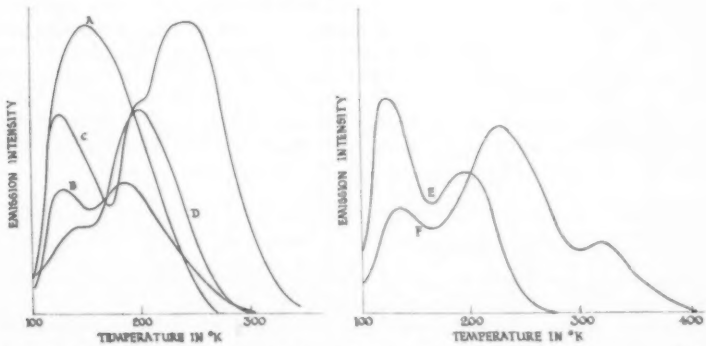

FIG. 2. Thermal glow curves of zinc sulfide phosphors after excitation at 90 K

A. ZnS-Zn (trace Cu)
B. ZnS-Ag
C. ZnS-Ag
D ZnS-Zn
E. ZnS-Mn (2%)
F. ZnS-Cu, specimen 1

Self-activated zinc sulfide phosphors: ZnS-Zn.—Self-activated phosphors having no traces of copper impurity show a stimulation spectrum consisting of one observable band beginning at about 1.3 μ and having its maximum in the visible region (not measurable). This spectrum decays

very rapidly in the dark at 90 K and seems to be associated with the shallowest electron traps, which likewise are emptied within a few minutes after excitation ceases. The emission during stimulation is blue. When traces of copper are present in such phosphors, an additional band appears in the stimulation spectrum having a maximum at 1.2 μ; its intensity is small compared with the main band of the spectrum. Stimulation in this new band still produces the characteristic blue emission of the phosphors. The band is enhanced by irradiation in the main band immediately before measurement in the 1.2 μ region. This effect is conveniently observed by traversing the monochromator from short wavelengths to long. In Fig. 1, the enhancing effect is seen by comparison of curves E and F, obtained by forward and reverse traversing, respectively. Other evidence, to be given later, leads us to infer that this enhancing effect is due to the retrapping of electrons in shallow traps after ejection from deeper traps. Thus the 1.2 μ band is associated mainly with the shallowest traps filled by excitation at the given low temperature. The light sum efficiency for irradiation in the 1.2 μ band of the spectrum is about 0.14.

Silver activated zinc sulfide phosphors: ZnS-Ag.—All silver activated phosphors containing no trace of copper show a single band in their stimulation spectrum with a maximum in the visible region (see Fig. 1). When traces of copper are present, the 1.2 μ band observed in the stimulation spectrum of self-activated phosphors appears and is again enhanced by previous irradiation in the main band at shorter wavelengths. In uncontaminated phosphors, stimulation at any wavelength in the main band tends to empty more shallow traps than deep ones. If the experiment is made at 180 K instead of 90 K, the spectrum is unaltered, but only traps which can retain electrons at this temperature are effective. When the 1.2 μ band is present, the decay of the stimulated emission is always more rapid for irradiation in this band than for irradiation in the main band. The optical light sum is also smaller for the 1.2 μ band.

Manganese activated zinc sulfide phosphors: ZnS-Mn.—When the manganese activator content of these phosphors is of the order of one or two per cent, the stimulation spectrum has one band, as shown in Fig. 1, curve G. The stimulated emission is always orange and characteristic of the activator. The electron traps are relatively shallow (Fig. 2), but there is little decay of the stimulation spectrum in the dark such as occurs in self-activated phosphors. When the manganese content is of the order of 0 01 per cent, the stimulated emission at low temperatures is blue and characteristic of self-activated specimens. The orange emission occurs feebly in specimens prepared at temperatures above 1000 C and is probably associated with the change of lattice structure to a wurtzite form. Stimulation causes ejection of electrons mainly from those traps which are associated with blue thermal glow emission, and only a small effect is observed on traps giving rise to orange thermal glow.

Copper activated zinc sulfide phosphors: ZnS-Cu.—We have studied copper activated phosphors of the long afterglow type having the wurtzite structure together with some other specimens having a blende structure or some special constitution. We find that the specimens which have a predominantly green emission at room temperature show green emission when stimulated at low temperatures. Other specimens, which have a

blue component in their emission, show predominantly blue emission, due to stimulation at low temperatures. In most cases, the stimulation spectrum consists of a main band with a maximum in the visible region and a subsidiary band with a maximum at 1.2 μ which we have already observed in phosphors contaminated by traces of copper. The relative heights of the two bands vary from specimen to specimen, having no definite relation to the thermal glow curves for the phosphors. Examples of these spectra are given in Fig. 1.

The enhancing of the 1.2 μ band by previous irradiation at shorter wavelengths is observed in these phosphors. In the case of specimen 1, direct evidence of the retrapping of electrons ejected by such irradiation was obtained. The experimental procedure, which we use for other phosphors described later, is as follows. The phosphor is excited at a tempera-

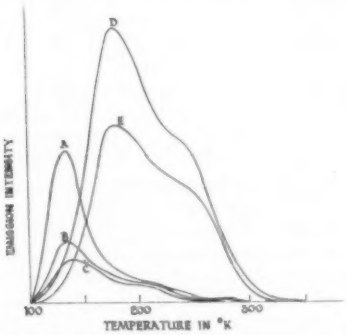

FIG. 3. Thermal glow curves of a ZnS-Cu phosphor showing effects of infrared radiation (excitation at 90 K).

A. Glow curve after 2 min decay at 90 K (blue emission)
B. Glow curve after 2 min irradiation at 90 K (1.2 μ, blue emission)
C. Glow curve after 2 min irradiation at 90 K (0.8 μ, blue emission)
D. Glow curve after 2 min decay at 90 K and after 2 min irradiation at 90 K (1.2 μ, green emission)
E. Glow curve after 2 min irradiation at 90 K (0.8 μ, green emission)

ture for which only electrons in deep traps are stable. It is then cooled suddenly and its thermal glow curve measured. The experiment is repeated, but this time the phosphor is irradiated by radiation of a suitable wavelength at the low temperature before measuring the thermal glow curve. Retrapping is then indicated by an enhancing of the glow curve at low temperatures where it previously had a zero value, or a much lower value (see Fig. 10).

All electron traps appear to be affected by stimulation, although the shallow ones are emptied preferentially. Compared with the main band of the stimulation spectrum, the 1.2 μ band is relatively ineffective in ejecting trapped electrons. In Fig. 3, we give thermal glow curves for a ZnS-Cu (0.01%) phosphor which has two emission bands, blue and green, at low temperatures. These curves show that irradiation reduces the thermal glow curves for the blue emission, but has much less effect on those for green emission. The 1.2 μ band hardly affects the latter at all.

Previous studies have shown that the green thermal glow emission is probably due to the proximity of the particular traps involved to the copper impurity centers and to their creation by the copper as activator. However, copper also produces the 1.2 μ band in the stimulation spectrum, which is effective only for traps associated with the blue emitting centers. In addition, the stimulated emission for all irradiation wavelengths is blue. These observations present an interesting theoretical problem.

General discussion of conventional zinc sulfide phosphors

We may note the common features in the infrared stimulation characteristics of all zinc sulfide phosphors at low temperatures. All specimens appear to possess a main spectral band for stimulation which extends well into the visible region and certainly overlaps the emission bands of the phosphors. Thus, at low temperatures, phosphors can be self-stimulated. At higher temperatures, it is probable that they are self-quenched. There is some evidence for this in studies made by A. F. Gibson, late of this laboratory. From the enhancing of the 1.2 μ band in these phosphors and from more direct evidence on one copper activated specimen, we infer that electrons ejected optically from traps can be retrapped in other and shallower traps, which may be empty. It is also evident that irradiation in the 1.2 μ band acts preferentially on shallow electron traps. All observations show that there is some definite connection between the trap distribution of a phosphor and its stimulation spectrum, but that the correlation is of a complex nature.

Infrared sensitive zinc sulfide phosphors

The properties of infrared sensitive phosphors, of the copper-lead activated type developed by Fonda, have been studied. Specimens were prepared with a wide range of copper and lead concentrations, the optimum concentrations for highest stimulability at room temperature agreeing with those reported by Urbach, *et al.* (0.001% Cu, 2–4% Pb). The lead was included as nitrate or sulfate. No flux was used, as its inclusion did not improve the stimulability of the phosphors. The specimens were fired in quartz tubes in air at temperatures between 950 and 1300 C. Fonda found that the emission spectrum for the fluorescence of these phosphors consisted of two broad bands, one in the blue-green region, the other in the yellow region, with maxima at 0.49 μ and 0.56 μ, respectively. Although a short-lived green afterglow occurred, the main afterglow was yellow. The stimulated emission was confined to the blue-green band.

The phosphors which we have prepared show rather different properties. The fluorescence emission may vary from blue-green to yellow depending on the constitution, mode of preparation, and phosphor temperature during observations. At room temperature, the afterglow has the same color as the fluorescence, and this is also true of the stimulated emission at room temperature. Stimulation tends to exhaust the green afterglow, leaving a yellow afterglow. We find, as Fonda did, that increase in the lead impurity tends to increase the yellow emission, but we also find that the same effect is produced by increase in copper content or firing temperature.

The thermal glow after excitation at low temperature is the same green as the fluorescence at room temperature for most of the phosphors. The peaks in the thermal glow curve are at the same temperatures as those in conventional phosphors, particularly copper activated specimens. The peak at the lowest temperature usually has the greatest intensity. Above room temperature, the thermal glow is small compared with that of ZnS-Cu phosphors (hexagonal form). The addition of lead to phosphors with the optimum copper concentration for long afterglow produces an enhancing of the room temperature stimulation, which is normally very small for these phosphors. The total light sum for thermal glow is of the same order for ZnS-Cu-Pb phosphors as for ZnS-Cu phosphors. The copper-lead activated phosphors are now considered in more detail.

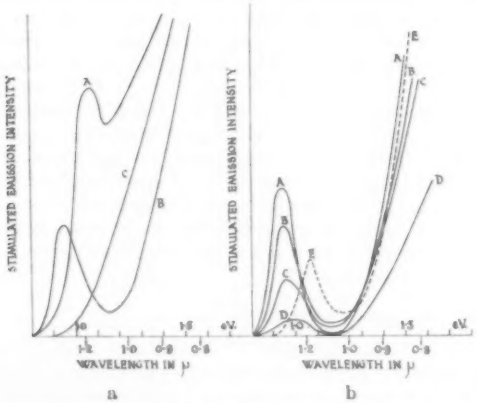

FIG. 4a. Stimulation spectra of ZnS-Cu-Pb phosphors at various temperatures after excitation at the same temperatures.

A. Specimen 3 at 77 K, B. specimen 3 at 290 K, C. specimen 2 at 77 K. Curve B is 4X correct magnitude compared with curve A.

FIG. 4b. Stimulation spectra of a ZnS-Cu-Pb phosphor (specimen 4)

A. Excited at 290 K, irradiated at 290 K
B. Excited at 290 K, irradiated at 260 K
C. Excited at 290 K, irradiated at 230 K
D. Excited at 290 K, irradiated at 200 K
E. Excited and irradiated at 90 K

At 77 to 90 K, the stimulation spectra of all ZnS-Cu-Pb phosphors are found to consist of a broad band beginning at 1.0 to 1.4 μ and extending into the visible region (at least to 0.6 μ), together with a sharp band at 1.2 μ, as shown in Fig. 4. We shall refer to these bands as the short and long wavelength bands, respectively, for the sake of brevity. Thermal glow curves, measured before and after infrared stimulation at 90 K, showed that 1.2 μ radiation usually ejected only the electrons in the shallower traps, while the short wavelength stimulation band was effective for these and often for deeper traps also. These effects are shown by the thermal glow curves of Fig. 5b for specimen number 6. In certain cases, infrared radiation can empty electron traps in such a way that groups of traps which normally contribute to a broad thermal glow peak

can be distinguished separately. This is shown by the curves of Fig. 5a for specimen number 1. In this case, 0.8 μ radiation does not remove electrons from traps responsible for the thermal glow at 100 K, but empties all other traps. The shallow traps can, however, be emptied by 1.2 μ radiation. This method of investigation can be used only when the trapped electrons all have lifetimes in the traps of several minutes, since a reasonable exposure to the stimulating radiation must be allowed. Stimulation associated with very shallow traps can, however, be studied by measuring the stimulation spectra after various times of decay in the dark after excitation. Such experiments showed that very shallow electron traps

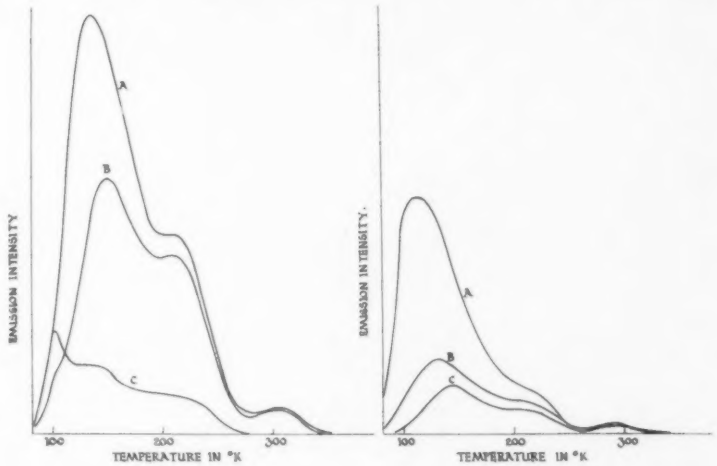

FIG. 5a. Thermal glow curves for a ZnS-Cu-Pb phosphor (specimen 1)

A. Excited at 77 K, decay in dark for 11 min
B. Excited at 77 K, irradiated at 1.2 μ for 12 min
C. Excited at 77 K, irradiated at 0.8 μ for 11 min

FIG. 5b. Thermal glow curves for the blue emission band of a ZnS-Cu-Pb phosphor (specimen 6).

A. Excited at 77 K, no irradiation
B. Excited at 77 K, irradiation at 1.2 μ
C. Excited at 77 K, irradiation at 0.9 μ

account for a large part of the stimulation in the 1.2 μ band at 77 to 90 K and, to a lesser extent, for the short wavelength band.

As already described for conventional phosphors, irradiation in the short wavelength band enhances the 1.2 μ band. Because of the association of the 1.2 μ band with the very shallow traps, we conclude that the enhancing is a result of retrapping of ejected electrons in these traps.

When the copper content is large, the stimulation spectrum of phosphors is similar to that already described. Specimen number 7 contained 2.10^{-3} copper and was fired at 1050 C. At 90 K, the fluorescence of this phosphor is blue (with a little green) in color, but becomes predominantly

green at 130 K. After the green emission decreases at about 220 K, an orange emission is visible up to 400 K. All three emission bands are present in the stimulated emission, due to irradiation in the short wavelength band. At 90 K, the 1.2 μ stimulation band gives rise to blue, and somewhat stronger green emission, but the orange emission is absent The stimulation spectra for the green and orange bands are given in Fig. 6. Fig. 7 shows the thermal glow curves obtained using filters to separate the curves for the different emission bands. Irradiation in the 1.2 μ band empties a few shallow traps operative in each of the glow curves for different emission bands. The blue and green thermal glow can be reduced greatly by 0.8 μ radiation while the orange component is hardly affected.

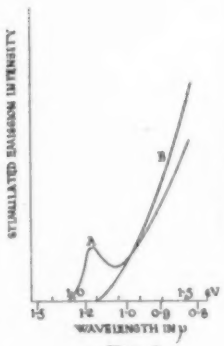

FIG. 6

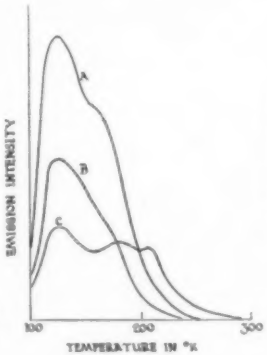

FIG. 7

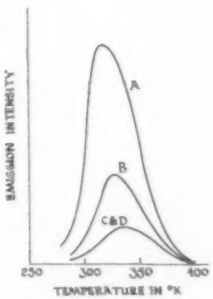

FIG. 8

FIG. 6. Stimulation spectra of a ZnS-Cu-Pb phosphor (specimen 7, high Cu conc)
A. Green emission B. yellow emission. Phosphor excited at 90 K

FIG. 7. Thermal glow curves of a ZnS-Cu-Pb phosphor (specimen 7, high Cu conc).
A. Green emission B. blue emission C. yellow emission. Curve C is 4X correct height

FIG. 8. Thermal glow curves of a ZnS-Cu-Pb phosphor (specimen 1)
A. Excited at 290 K, decay in dark for 1 min
B. Excited at 290 K, irradiated at 1.05 μ for 1 min
C. Excited at 290 K, irradiated at 1.3 μ for 1 min
D. Excited at 290 K, irradiated at 0.8 μ for 1 min

We give this phosphor as an example because of these different effects for the different emission bands.

Phosphors having lead and copper contents not greatly different from the optimum values show strong stimulation at room temperature; the stimulability is of the same order as that at low temperatures. The stimulation spectrum at room temperature agrees with that already given by other workers, namely, a sharp band at 1.3 μ and a broad band extending from about 1 μ into the visible region, as shown in Fig. 4. Phosphors with high copper concentrations show little stimulability above 90 K and the 1.3 μ band does not appear.

In Fig. 8, we give thermal glow curves of a ZnS-Cu-Pb phosphor ex-

cited at room temperature, which show how the ejection of trapped electrons depends on the wavelength of the infrared radiation. For wavelengths lying between the main stimulation bands, the ejection efficiency is low, although the radiation intensity is near its maximum in this region.

Temperature dependence of stimulation, etc.—When phosphors showing the characteristic high temperature stimulation spectrum are excited at room temperature, cooled to 77 K, and then irradiated, no stimulation is observed. However, if the temperature is raised, stimulation due to irradiation in the short wavelength band is observed above about 80 to 130 K (depending on the particular phosphor), and stimulation due to 1.3 μ radiation occurs above 160 to 180 K. The position of the maximum of the 1.3 μ band remains the same over the temperature range in which

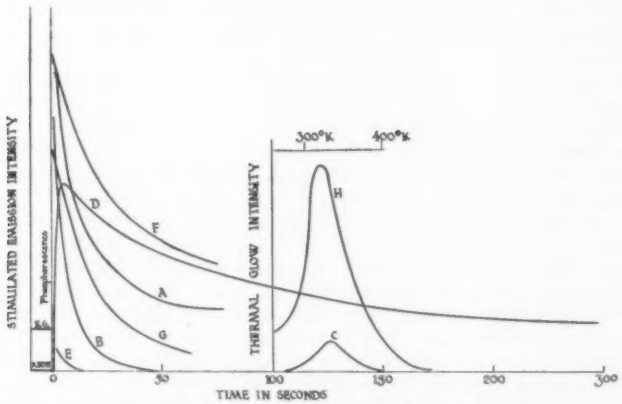

FIG. 9. Decay curves of stimulated emission and thermal glow curves for ZnS-Cu-Pb phosphors excited at 290 K.

A. Specimen 1, 0.8 μ irradiation
B. Specimen 1, 1.3 μ irradiation
C. Glow curve after excitation and decay in dark for 1 min (specimen 1)
D. Specimen 2, 0.8 μ irradiation
E. Specimen 2, 1.3 μ irradiation
F. Specimen 3, 0.8 μ irradiation
G. Specimen 3, 1.3 μ irradiation
H. Glow curve after excitation and decay in dark for 1 min (specimen 3)

stimulation is possible (see Fig. 4b). As the bands retain their form and position with change of temperature, the temperatures at which stimulation was possible are determined as follows. The phosphor is excited at room temperature and cooled to liquid air temperature. The phosphor is then irradiated with suitable radiation (e.g., 1.3 μ) and then warmed, the irradiation remaining constant, and the emission recorded continuously.

By comparing with a control experiment having no irradiation present, the approximate temperature at which stimulation is possible can be approximately found. This "rise temperature" is found to be the same for excitation at temperatures higher than room temperatures, provided that the latter are not too high for stimulation without cooling. It is also found that, for stimulation at the same temperature as excitation, the stimulation spectra depend in a similar way on temperature. In the region

between 180 and 440 K, the 1.3 μ band is strong. Phosphors excited at 180 K show stimulation for irradiation in the short wavelength band at 77 to 90 K, although no stimulation occurs for such irradiation after excitation at room temperature.

Optical light sums and decay of stimulated emission.—The optical light sums produced by stimulation in the two different spectral bands are different (at 290 K). A greater light sum is always obtained for irradiation by wavelengths in the short wavelength band. If the irradiation is such that the initial stimulated emission is of the same intensity for long and short wavelength infrared, then the decay for 1.3 μ radiation is more rapid than that for shorter wavelengths; it also may be of a different form, as shown by Fig. 9. Specimen number 1 shows a decay of stimulated emission which is exponential over most of its range (curve B). Most of the other decay curves measured very closely approximated hyperbolic form. (Under heterochromatic irradiation, Fonda (3) has reported exponential decays, and Urbach, *et al.* (6) have reported hyperbolic decays. Their results may be due to superposition of two decay curves, each of a complex nature. The above observations stress the need for monochromatic irradiation when measuring the decay of stimulated emission.)

The optical light sums are at least equal to, and usually much greater than, the thermal light sum obtained for similar excitation. These differences cannot be attributed to changes in emission spectra and their effect on the recording system in our experiments. In specimen 2, the optical light sum for 0.8 μ irradiation is at least 400 times the thermal light sum. The large differences in light sums cannot be attributed to fall in luminescence efficiency at higher temperatures where thermal glow is still present, unless the efficiency for thermoluminescence is essentially different from that for fluorescence. One or two other observations are important here. It is usually found that after the stimulated emission due to 1.3 μ radiation has decayed to a low value, strong stimulation of long duration can still be obtained with shorter wavelength infrared radiation (0.8 μ). At room temperature, it is found for specimens 1 and 2 that 1.3 μ radiation reduces considerably the intensities of both stimulation bands. Irradiation with 0.8 μ radiation produces a similar, but less marked, effect. For specimen number 5, the intensity of the maximum of the curve for the variation of stimulated emission with temperature does not vary by more than 50 per cent when the temperature of excitation changes from 250 to 320 K (0.8 μ irradiation). However, the change in the thermal light sum over this range is more than fiftyfold.

From the above data, it would seem that the thermoluminescence curve does not represent the true trap distribution. We must infer that the probability of nonradiative loss of the energy of electrons released from traps is different from that for electrons taking part in fluorescence processes.

Retrapping during stimulation processes.—In all cases where it was possible to carry out the test for retrapping of electrons ejected by stimulation, retrapping was found to occur (see "Experimental Techniques" for description of experimental method). We established that the retrapping effects were not due to excitation of the phosphor by stray light in the apparatus from the monochromator. The main difficulty in carrying out the experiment on all specimens is that, when a phosphor is excited

at a given high temperature and then cooled to the selected low temperature at which electrons retrapped are stable, the electrons trapped initially may not be ejected by irradiation. This is due to the temperature dependence of stimulation described above. Retrapping occurs in shallow traps when electrons are ejected at 90 K from traps stable at 180 K (after excitation at 180 K) when 0.8 μ radiation is applied. Similar retrapping occurs at 180 K when electrons are ejected from traps stable at 290 K (excitation at 290 K).

It is found for specimen number 5 that the thermal light sum for the retrapped electrons is about six times that for the original distribution of trapped electrons as shown in Fig. 10. This effect is obviously associated with the differences between optical and thermal light sums already discussed above. Several workers have reported that, on irradiation of infra-

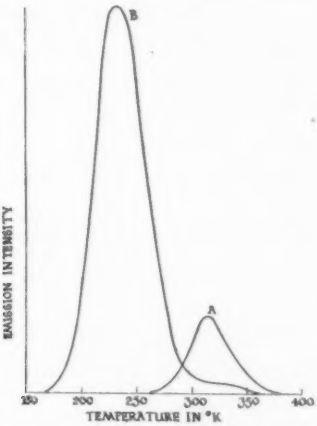

FIG. 10. Thermal glow curves for a ZnS-Cu-Pb phosphor (specimen 5) showing the effect of retrapping.

A. Glow curve after excitation at 290 K and cooling in dark to 150 K
B. Glow curve after excitation at 290 K and irradiation by 0.8 μ at 90–180 K

red sensitive phosphors, the stimulated emission takes some time to reach its maximum value. They are probably correct in attributing this effect to retrapping, but their findings could always be explained by a two-stage process of stimulation, one stage having a low probability. Fig. 9 includes an example of this slow rise process (curve D). Our experiments have provided more definite evidence for retrapping in many different phosphors when stimulation occurs.

The long wavelength stimulation bands in ZnS-Cu-Pb phosphors.—There is no doubt, as Fig. 4a and 4b show, that the 1.2 μ low temperature band and the 1.3 μ room temperature band of the stimulation spectrum of these phosphors are quite distinct. Their position does not vary with temperature so that one band cannot be explained as a due-to-temperature-shift of the other. We suggest that they arise from two different absorbing

systems in the phosphors and that their proximity is fortuitous. It is of interest to note the small half width of these bands, which is less than 0.15 eV, even when the 0.06 eV monochromator beam width is included. We shall discuss this further in the last section.

A summary of the main results for ZnS-Cu-Pb phosphors is included in Table I.

TABLE I. *Characteristics of copper-lead activated zinc sulfide phosphors*

Specimen no.	1	2	3	4	5	6
Cu conc	9.10^{-6}	9.10^{-6}	9.10^{-6}	4.10^{-6}	5.10^{-6}	9.10^{-6}
Pb conc	4% $PbSO_4$	4% $PbSO_4$	4% Pb $(NO_3)_2$	6% Pb $(NO_3)_2$	4% Pb $(NO_3)_2$	4% Pb $(NO_3)_2$
Firing temp	1050 C	1050 C	1050 C	1050 C	1250 C	1050 C
Color of fluorescence at 290 K	Blue-green	Yellow-green	Blue-green	Blue-green	Blue-green	Blue-green
Yellow phosphor after stimulation	Absent	Absent	Present	Present	Absent	Absent
Temp thermal glow peaks K	(100), 140, 220, 310	115, 170, 240	140, 220, 310	140, 220, 310	110, 140, 220	140, 220, 320
1.2 μ stimulation at 77 K	Strong	Absent	Very strong	—	Moderate	—
90 K	Moderate	Absent	Weak	Strong	Weak	Moderate
Dark decay of stimulation at 77 K	Rapid	Slow	Rapid	Rapid	Slow	Rapid
90 K	Slow	Slow	Slow	Rapid	Rapid	Rapid
1.2 μ band						
Minimum stimulation temp for 1.3 μ radiation excited at 290 K	160 K	180 K	160 K	180 K	180 K	170 K
Minimum stimulation temp for main band, excited at 290 K	100 K	80 K	100 K	100 K	100 K	130 K
Light sums, excited at 290 K arb. u.						
Optical, 0.8 μ	>120	>400	>1000		>60	
Optical, 1.3 μ	30	2	100		4	
Thermal	4	<1	60		4	

Conventional alkaline earth sulfide phosphors

Although our investigations of the copper-lead activated zinc sulfide phosphor emphasize the danger of generalizing from results obtained on a few phosphors, we have been forced to investigate but a few conventional alkaline earth sulfide phosphors because of their poor stimulability. The only phosphors of interest have been bismuth and lead activated calcium sulfide. The latter, of which one good specimen was available, possesses few electron traps stable at room temperature. The glow curve consists of four peaks below room temperature. Considerable stimulation occurs at 90 K by wavelengths less than 1.5 μ; the stimulation spectrum rises at this wavelength and increases in intensity into the visible region. All glow curve peaks except the highest temperature peak are reduced by irradiation in the broad stimulation band.

All CaS-Bi phosphors show good stimulation at room temperature and optical light sums are quite large. Most phosphors have very similar glow

curves (see Fig. 11) with a sharp peak at 80 to 100 K and a broad peak at 400 K; some weaker peaks may occur at even higher temperatures. However, the stimulability of a phosphor shows no correlation with its thermal glow curve. Specimens with comparatively weak thermal glow often show strong stimulation. All specimens of CaS-Bi phosphors are found to show blue-violet emission under stimulation. No evidence of other bands has been obtained in the absence of deliberate impurity other than bismuth. A few specimens are considered in detail:

Specimen 1. CaS-Bi.—The deeper traps in this phosphor are not filled by excitation at low temperatures. As shown in Fig. 11, the peak at 340 K is much weaker when excitation is at 77 K than when it is at 290 K. Similarly, another peak at 540 K is not present if excitation is carried out

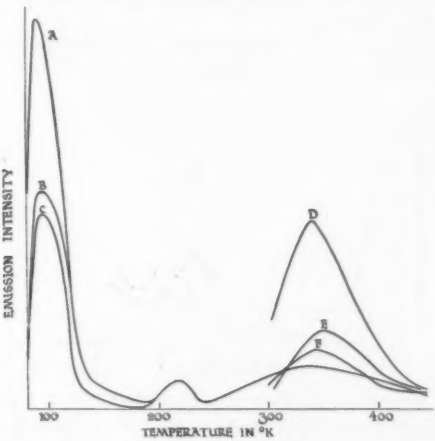

FIG. 11. Thermal glow curves of a CaS-Bi phosphor (specimen 1)

A. Excitation at 77 K, no irradiation
B. Excitation at 77 K, irradiation at 1.0 μ
C. Excitation at 77 K, irradiation at 0.75 μ
D. Excitation at 290 K, no irradiation
E. Excitation at 290 K, irradiation at 1.0 μ
F. Excitation at 290 K, irradiation at 0.75 μ

at 77 K and does not attain its full height for any temperature of excitation below 450 K. (A similar effect was observed in thallium activated alkali halide phosphors by Randall and Wilkins, and in $ZnBeSiO_4$-Mn-Sn by us.) The stimulation spectrum of the above phosphor consisted of bands with maxima at 0.97 μ, 0.76 μ, and in the visible region. There is a long wavelength tail which extends to 1.7 μ as shown in Fig. 12. This tail only occurs for excitation at 77 K, and even then does not appear if only 0.365 μ excitation is used. Fig. 12 shows the dependence of the stimulation spectrum on the excitation temperature. Comparison with the thermal glow curves of Fig. 11 shows that the filling of deep traps enhances the 0.76 μ peak. Since warming to 140 K, followed by cooling again to 90 K, does not reduce the spectrum appreciably, we may assume that deeper traps are mainly responsible for the stimulation under these conditions, except for the stimulation in the long wavelength tail of the spectrum.

After excitation at a high temperature, the stimulability of the phos-

phor depends markedly on the temperature. After excitation at 390 K, the band at 0.76 μ is about ten times greater at 77 K than at 245 K. After excitation at 77 K, only the thermal glow curve peak at 87 K is lowered to any extent by stimulation. In this respect, 0.75 μ radiation is more effective than 1.0 μ radiation, as shown in Fig. 11. This is generally so for excitation at higher temperatures also. However, after excitation at 290 K, the irradiation at 77 K in the region of 1.0 μ preferentially reduces the height of the 0.97 μ band, and irradiation in the region of 0.75 μ reduces that of the 0.76 μ band. There is, thus, no direct association between a particular stimulation band and a particular thermal glow peak, although the intensity of the 0.76 μ band is enhanced when deeper traps are filled. When traps are filled by excitation at 290 K, irradiation by 0.76 μ radiation at 77 K fills traps giving the thermal glow peak at 87 K by the retrapping of ejected electrons.

Specimen 2. CaS-Bi.—The stimulation and thermoluminescence characteristics of this phosphor are similar to those of specimen number 1,

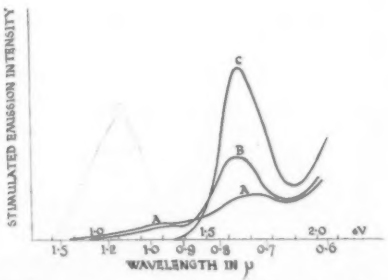

FIG. 12. Stimulation spectra of a CaS-Bi phosphor (specimen 1)

A. Spectrum at 77 K, excitation at 77 K C. Spectrum at 77 K, excitation at 453 K
B. Spectrum at 77 K, excitation at 290 K

except that the deep traps are effectively filled at all temperatures of excitation.

Specimen 3. CaS-Bi.—Although this specimen has the usual thermal glow of this type of phosphor, it shows very weak stimulation at room temperature or at low temperatures after room temperature excitation. The stimulation spectrum begins at about 1.4 μ and increases in intensity toward shorter wavelengths. After excitation at 77 K, a similar spectrum is obtained, but it begins at 1.6 μ and the stimulability is much greater than that at room temperature.

Infrared sensitive alkaline earth sulfide phosphors

Extensive work by Urbach and others (1) has shown that the main properties of doubly activated alkaline earth sulfide phosphors are as follows:

The stimulated emission is characteristic of the dominant activator, while the stimulation spectrum is characteristic of the auxiliary activator. In SrS and CaS, the most effective dominant activators are Ce, Cu, Eu, and Mn, while the most effective auxiliary activators are Bi and Sm. The

thermoluminescence emission spectrum may be due to either dominant or auxiliary activators. Absorption measurements made on SrS-Eu-Sm in the excited and unexcited states showed distinct differences. The absorption in the unexcited phosphor, in a band due to the dominant activator, decreases on exciting the phosphor, the decrease being more marked when the auxiliary activator concentration is increased. Absorption in this region excites the phosphor. When excited, the phosphor possesses new absorption bands in the visible and infrared, which have been attributed to the auxiliary activator. Absorption in these bands increases with auxiliary activator concentration and also may give rise to stimulation.

We now consider our own experimental results for this type of phosphor. We were limited to three specimens supplied by Prof. Ward, but

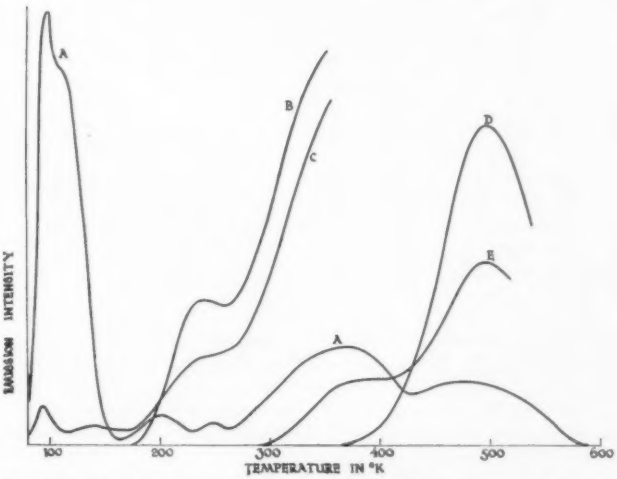

FIG. 13. Thermal glow curves for St. VII phosphor showing effects of retrapping.

A. Glow curve after excitation at 77 K
B. Glow curve after excitation at 180 K
C. Glow curve after excitation at 180 K and irradiation at 77 K (0.6 μ)
D. Glow curve after excitation at 418 K
E. Glow curve after excitation at 418 K and irradiation at 290 K (1.0 μ)

our results are of considerable interest for each particular specimen. It is difficult to make general deductions from results obtained with so few specimens, but significant correlation with the results for other phosphor types above will be evident.

Standard VII phosphor, SrS-Ce-Sm.—The stimulated emission of this phosphor is blue-green and characteristic of the dominant activator cerium. According to Urbach and others (1), the emission spectrum consists of two bands with maxima at 0.48 μ and 0.54 μ. The line spectrum of samarium appears in the thermal glow or fluorescence at high temperatures. The thermoluminescence curve we obtain for this specimen after excitation at 77 K is given in Fig. 13. Emission in all bands of the curve below room temperature is blue-green, in the peak at 370 K is partly

blue-green and partly orange (Sm), while in the peak at 480 K it is entirely orange. After excitation at a temperature above 170 K, the stimulation spectrum is found to contain two bands, a broad band with a maximum at 1.0 μ and a band rising at about 0.75 μ and increasing in intensity into the visible region. The 1.0 μ band is presumably that reported previously by other workers; the short wavelength band may correspond to the absorption band which has a maximum at 0.57 μ and which appears when phosphors with samarium as auxiliary activator are excited. After excitation at a given temperature, the stimulation spectrum at a lower

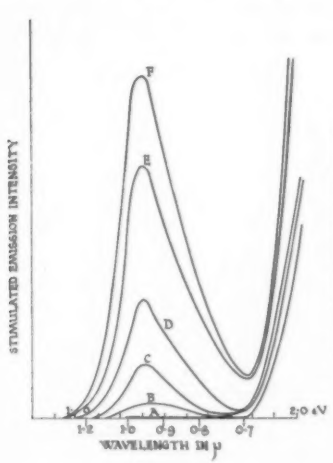

FIG. 14

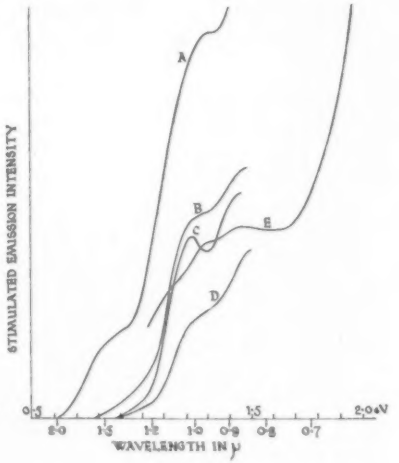

FIG. 15

FIG. 14. Stimulation spectra of a SrS-Ce-Sm phosphor at various temperatures after excitation at 290 K.

A. 77 K
B. 123 K
C. 152 K
D. 180 K
E. 225 K
F. 270 K

FIG. 15. Stimulation spectra of St. VII phosphor excited at 77 K after 3 min irradiation at various wavelengths.

A. No irradiation
B. Irradiation at 1.6 μ
C. Irradiation at 1.3 μ
D. Irradiation at 1.1 μ
E. No irradiation, blue emission only

temperature is found to be markedly dependent on the temperature. The blue emission component of the stimulation spectrum at various temperatures, after excitation at 290 K, is given in Fig. 14. It will be seen that, over the range studied, the short wavelength band is much less dependent on temperature than the 1.0 μ band. The shift of the maximum of the 1.0 μ band shown in the figure is due to the time lag effect described in "Experimental Techniques."

It is now necessary to distinguish between variations of the stimulation spectrum, due to changes in the population of traps, with the excitation temperature, and those due to changes in the stimulability of a given population of filled traps with temperature. Experiments have been made

in which the stimulation spectrum at a given temperature is determined for various temperatures of excitation above the given temperature. These sets of experiments are repeated using different temperatures of stimulation. In this way, it can be shown that the filling of shallower traps increases the height of the 1.0 μ band at the stimulation temperature over the whole available temperature range. (We may recall that the emission spectrum of thermal glow due to shallow traps is different from that due to deep traps.) For temperatures of excitation below about 290 K, the 1.0 μ band appears with reasonable intensity at 77 K.

The stimulation spectrum obtained after excitation at 77 K is more complex than that described above; it is given in Fig. 15. Irradiation at various wavelengths which produce stimulation produces a preferential reduction of various parts of the stimulation spectrum. In this way, it is possible to identify the various bands present in a complex stimulation spectrum. Besides the bands which appear at high temperatures (at 1.0 μ and in visible), there are probably bands at 1.5 μ and 0.85 μ. These new bands may each be due to several bands.

We now consider the way in which the distribution of trapped electrons is changed during stimulation. We cannot obtain accurate data with this phosphor since the light sums are so great that little lowering of the thermal glow peaks at high temperatures occurs in a reasonable time with the weak monochromatic infrared radiation available. The effect of irradiation, after excitation of the phosphor at 77 K, is first described. Irradiation by 1.5 μ radiation produces a lowering of the glow peak at 100 K only, while 1.0 μ and 0.6 μ radiation reduces the height of all glow peaks, but mainly those at lower temperatures. After excitation at 290 K, irradiation at 1.0 μ lowers the height of the peak at 480 K more than that of the peak at 370 K. Unfortunately, we have no reliable data for the effect of 1.0 μ radiation at 77 K on traps filled at 290 K. Any considerable ejection under these conditions would indicate that electrons removed from traps by irradiation lose their energy nonradiatively, since no stimulated emission is observed. The alternative hypothesis, that the presence of electrons in shallow traps affects the deeper traps so that they can be emptied at lower temperatures, is more probable.

The height of the stimulation spectrum at 77 K decreases markedly after decay in the dark for several minutes, indicating that shallow traps are at least partly responsible for stimulation in the 1.0 μ band at this temperature. Electrons removed from deep traps by stimulation can be retrapped in shallow traps, in which they are stable at the stimulation temperature. Examples are given in Fig. 13.

If this phosphor is excited by 0.36 μ radiation, the stimulation is very feeble. No stimulation is observed after excitation at 77 K, and that at 290 K is very much less than that for shorter wavelength excitation. The heights of the glow curves are correspondingly smaller.

Standard VI, SrS-Eu-Sm.—Because of the poor response of the photomultiplier to the red emission of this phosphor, we have not made a full study of this phosphor. It is possible to confirm the stimulation spectrum and thermal glow curve reported by Urbach (4) for room temperature excitation of the phosphor. (The maximum of the infrared stimulation band is at 1.0 μ; the glow curve rises at 420 K and extends beyond 600 K.) After excitation at 90 K, thermal glow peaks occur at 120, 140, and 200 K.

The glow peak at the high temperature cannot be detected after low temperature excitation. After excitation at 90 K, no stimulation is observed after subsequent heating to 300 K. As a comparison, Urbach found that the thermal light sum, obtained after excitation of such a phosphor at different temperatures, was greater for excitation at 213 K than for that at 77 K. For higher excitation temperatures, the thermal light sum is approximately constant until temperatures are reached at which the trapped electrons still stored become unstable.

B.I phosphor, SrSeS-Eu-Sm.—This phosphor has a yellow emission characteristic of europium in a SrSeS lattice. After excitation at 77 K,

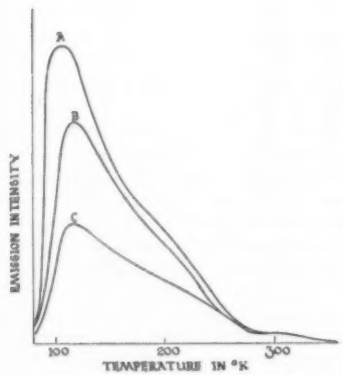

FIG. 16

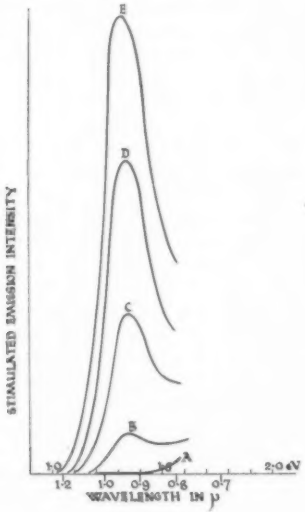

FIG. 17

FIG. 16. Thermal glow curves for B.I phosphor excited at 77 K

A. No irradiation
B. After irradiation at 1.6 μ
C. After irradiation at 0.94 μ

FIG. 17. Stimulation spectra of B.I phosphor excited at 360 K

A. Stimulation at 90 K
B. Stimulation at 130 K
C. Stimulation at 154 K
D. Stimulation at 174 K
E. Stimulation at 195 K

the thermal glow is yellow at low temperatures (see Fig. 16). However, if the phosphor is excited at room temperature or above, no thermal glow can be detected at temperatures below 600 K. Since strong stimulation occurs at room temperature after excitation, it must be assumed that there are traps capable of storing the electrons responsible and they are stable when filled at this temperature. It may be that emission occurs in the infrared, but this is rather unlikely. Europium and samarium have their emission in the visible in this phosphor and, in each case, it is little affected by the center environment. The energy of the electrons ejected from traps by thermal motion is most likely dissipated nonradiatively.

After excitation at room temperature, the intensity of the stimulated emission is found to vary markedly with the temperature of stimulation. The stimulation spectrum consists of a band with a maximum at 0.93 μ and a band which extends into the visible region. Similar temperature dependence of stimulation is found at high excitation temperatures; this dependence is shown by the curves of Fig. 17. It is found that the variation of stimulated emission with temperature under constant irradiation (0.94 μ) has a similar form for various excitation temperatures, but the maximum intensity reached varies with the excitation temperature. After excitation at 290 K, the maximum intensity occurs at 220 K. The highest maximum was reached for excitation at 290 K. The intensity of stimulation decreases rapidly for excitation temperatures above 450 K and no stimulation is observed at any temperature after excitation at 550 K. It is, therefore, probable that the depths of the traps involved would normally be associated with thermoluminescence between 300 K and 550 K. After excitation at 77 K, stimulation is produced by radiation of wavelengths less than 2.3 μ. After four minutes decay in the dark at this temperature, no stimulation is observed for irradiation of wavelengths greater than 1.8 μ. In Fig. 16 we give the thermal glow curves after stimulation by radiation of different wavelengths and for excitation at 77 K, which show that 1.6 μ radiation empties mainly the shallow traps, while 0.94 μ radiation also empties the deeper traps.

After excitation at 77 K by 0.43 μ and 0.40 μ radiation, no stimulation is observed at long wavelengths. The thermal glow curve for such excitation is similar to curve C of Fig. 16. The height of the peak at 120 K is reduced by 0.94 μ radiation. After similar excitation at 290 K, the stimulation spectrum has the same intensity as that obtained with the usual excitation wavelengths (0.25–0.37 μ). The fluorescence of this phosphor under excitation is poor, but its efficiency is greatly increased if infrared radiation is present; it shows no great reduction until a temperature of 470 K is reached.

DISCUSSION AND CONCLUSION

We may summarize the general results of our studies as follows:

1. There appears to be no simple relation between the electron trap distributions of phosphors, the stimulability, and the stimulation spectrum.

2. It is usually found that, at a given temperature, long wavelength bands of the stimulation spectrum are less effective for ejection of electrons from deeper traps than shorter wavelength bands. The long wavelength bands appear to act preferentially on shallow traps, whatever the excitation temperature and population of the traps.

3. In some phosphors, infrared radiation of a given wavelength can act selectively on traps which give rise to a single band in the thermal glow curve, thus showing that the band is due to distinct groups of electron traps which would otherwise be unresolved in the thermal glow curve experiments (see Fig. 5a).

4. The stimulation spectrum of all phosphors studied above consists of a main band with its maximum in the visible, and there is no doubt that the band overlaps bands in the emission spectrum of many phosphors. Other bands of smaller intensity occur at longer wavelengths and appear

to be related to a particular activating impurity (e.g., Sm gives 1.0 μ band in SrS; Cu gives 1.2 μ band at low temperatures in ZnS).

5. When phosphors are stimulated, the optical light sum is hardly ever equal to the thermal light sum. In conventional phosphors, it is usually smaller than the thermal light sum, but in infrared sensitive phosphors, it may be a hundred times as great.

6. The decay of the stimulated emission with time follows a different relation for each stimulation band. In some cases, such as in certain ZnS-Cu-Pb phosphors and for suitable wavelength of stimulating radiation, it is exponential in form but, in general, the decay has a hyperbolic form.

7. The experimental results provide direct evidence for retrapping of electrons in shallow traps subsequent to their release from deep traps by stimulation. In some cases, the thermal glow curve and the light sum are much greater after stimulation than before (see Fig. 10).

8. The special infrared sensitive phosphors excited at a particular temperature may not be stimulated at temperatures below a certain minimum temperature, which is dependent on the particular stimulation wavelength and on the excitation temperature. The long wavelength bands of the stimulation spectrum have the highest minimum temperatures.

The above summary of results indicates a formidable theoretical problem. We may, however, make a few theoretical deductions of a relatively simple nature as follows:

1. Absorption of radiation causing stimulation appears to take place in definite "centers," quite distinct from the emission centers and from the electron traps. However, these centers must have interaction with the emission centers and traps, since absorption is observed only when the phosphor is excited, that is, when emission centers are emptied and traps filled by electrons. We suggest that, after absorption, these centers, in their excited state, perturb the electron trap configurations by vibrational interaction with them, so that the traps are made effectively shallower and lose their electrons. Such interaction of the excited absorbing centers must also occur in order to account for the large differences between optical and thermal light sums; this interaction may also account for the low luminescence efficiency of infrared sensitive alkaline earth sulfide phosphors during excitation and in the absence of stimulating radiation.

2. The existence of a minimum temperature for stimulation, after excitation of phosphors at higher temperatures, indicates that even when interaction takes place, as assumed above, the electron traps which are perturbed still possess a finite depth and so an activation of a thermal nature is still necessary. It follows from our results that the activation energy is smaller for the shallower traps, which would be expected, since lowering of the temperature of excitation lowers the minimum temperature.

3. Retrapping does not usually occur after the thermal release of trapped electrons (2), and our previous studies indicate that this is explained by the coexistence of emission centers and traps in larger complexes in the phosphor with the impurity activators as nuclei. Retrapping after optical ejection of trapped electrons may be explained by their ejection into the matrix conduction band; this might be investigated by means of photoconductivity experiments. It is more probable that the perturbation of

trap configurations discussed above is closely connected with the occurrence of retrapping. More evidence is required to obtain a clearer idea of the cause of retrapping. The enhancing of the thermal light sum after retrapping is also to be correlated with the perturbation.

4. The half width of some bands in the stimulation spectrum (e.g., 1.2 μ band in ZnS-Cu and 1.3 μ band in ZnS-Cu-Pb) is found to be less than that for F center absorption bands in the alkali halides. Thus, the singularity responsible for the stimulation bands must be relatively well defined. We might expect that it would not only absorb, but also emit characteristic radiation. If it functions as an excited center without losing an electron, then we would expect absorption to occur even at temperatures below the minimum temperature for stimulation in the particular band. We have not made absorption measurements to test this assumption.

In conclusion, we suggest that the failure of the stimulation characteristics of phosphors to fit the existing theoretical models for phosphors demands a much more precise experimental approach than has hitherto been made. It is essential to make absorption measurements at long wavelengths on excited phosphors over wide ranges of temperature and excitation conditions. Any theoretical model proposed for the above properties of phosphors must also be able to explain why certain phosphors with many traps, such as Zn_2SiO_4-Mn-As, cannot be stimulated by radiation of longer wavelengths than those giving rise to excitation. Finally we wish to reiterate Urbach's (4) suggestion that experiments should be carried out on much simpler systems than those investigated above. In particular, they should be made on materials which are available as good homogeneous crystals of reasonable dimensions.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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DIFFERENTIAL THERMAL ANALYSIS STUDIES IN SOME SILICATE SYSTEMS[1]

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ABSTRACT

The method of differential thermal analysis has been applied to the qualitative study of the reaction processes in the formation of some zinc silicate phosphors. Heating curves are given showing how the various reactions may be identified, and illustrating the effects of small additions of beryllium, manganese, and potassium compounds. The evidence for the formation of intermediate phases and their effects on the reaction mechanism is discussed. The luminescence of some intermediate phases is mentioned.

INTRODUCTION

In discussions on the synthesis of substituted zinc silicate phosphors, it has often been tacitly assumed that the reaction proceeds by the formation of the separate silicates, for example, of zinc, beryllium, and manganese, followed by their mutual solution. In this example, the rate limiting process was generally supposed to be the diffusion of beryllium silicate into the zinc silicate lattice. It is now thought that such a picture is greatly over-simplified (1) although experimental evidence for other mechanisms has not been widely discussed.

Taking zinc beryllium silicate as an example, it was observed in this laboratory, several years ago, that the changes in the color of the fluorescence took an unexpected course as reaction proceeded. The first luminescence to appear was always green, but the final fluorescence was reached via a color richer in red than the ultimate color. The color change from green to red was a rapid process, while the further change from red to yellow was much slower.

Some later experiments dealt with the synthesis of substituted zinc silicate phosphors in stages. The reaction mixture, with one or more of the components omitted, was given an initial heating, and the other components were added in a second or subsequent heating. In the case of one such addition, potassium carbonate, where it was desired to obtain a zinc beryllium potassium silicate, a material having particular practical advantages, it was found essential that this be added either at the same time as the zinc oxide, or at a subsequent stage. If the opposite order were followed, the final product was never completely combined, in spite of prolonged heating.

Such results prompted a more detailed investigation of the reactions in these systems. The present paper discusses information obtained by the use of differential thermal analysis.

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EXPERIMENTAL

It is not proposed to give a detailed description of the apparatus, since it embodies no unusual features. The samples were packed in alumina crucibles of 1 ml capacity. A chromel-alumel differential thermocouple was used for measuring the temperature difference between the sample and the reference material, and a rare-metal thermocouple recorded the furnace temperature. The rate of temperature rise was approximately 10 C per minute in all experiments. Ignited alumina was used as reference material, and all the temperatures mentioned in the discussion relate to this material. It is better to correct peak temperatures to those of the sample itself, but, in this case, the differences introduced are too small to invalidate the conclusions based on the less rigorous method.

Since the origin and methods of preparation of the individual reactants must obviously affect the reactions observed, as has been very fully discussed by J. A. Hedvall (2), a brief description of the materials used and the methods of preparing the samples is necessary.

Zinc oxide was obtained by precipitation of a purified solution of zinc nitrate, through which carbon dioxide was passed, with a solution of ammonium carbonate. After washing, the precipitate was dried at 250–300 C for 16 hours, when most of the carbonate was decomposed.

Beryllium was added to the mixtures as a very pure grade of the hydroxide.

Silica was in the form of a fine silica gel. It was purified by boiling with strong hydrochloric acid, followed by washing until the filtrate was free from chloride. The product was dried at about 250 C.

In mixtures containing manganese and/or potassium, these were added as solutions. Manganous nitrate was added as a solution containing approximately 0.1 gram of manganese per ml, while potassium carbonate was added as a 10 per cent solution. The mixtures were made into a creamy paste, using more distilled water if necessary, and the paste dried out for 16 hours at 250 C, at which temperature the manganous nitrate was entirely decomposed to a black oxide, principally the dioxide. The dried cake was then thoroughly ground in a mortar.

When neither manganese nor potassium carbonate were required in the mixture, the other constituents were simply ground together in the dry state. Since in all cases the samples were quite small, intimate mixing could be achieved in this way.

Where starting materials other than those described above were used, particulars are given in the text.

EXPERIMENTAL RESULTS

In nearly all the heating curves there were two groups of peaks. The first of these was an endothermic group, occurring between room temperature and 350 C and due to loss of moisture, thermal decomposition of traces of carbonate, hydroxide, etc., in the zinc oxide, and decomposition of the beryllium hydroxide. These peaks were extremely large, making it impracticable to reproduce them in diagrams in which the second group of peaks could be given on a reasonable scale. Since it is this second group which most concerns us, the heating curves reproduced here omit the low temperature effects.

Apart from this omission, the usual conventions are used, exothermic reactions being represented by displacements of the curves in a positive direction relative to the temperature axis.

The main results are given in the heating curves of Fig. 1 and 4. These heating curves show the changes in the reaction between zinc oxide and silica, caused by the introduction of manganese dioxide, potassium carbonate, and beryllium oxide, either singly or in association. Details of the reaction mixture accompany each curve.

The ZnO-SiO_2 system (Fig. 1: First curve).—The formation of zinc silicate occurs as an exothermic reaction beginning at 800 C and slowly reaching a peak at 935 C. The exothermic process with a peak at 370 C s probably due to an adsorption effect. In a study of the catalytic activty of heated mixtures of zinc oxide and silica, Jander and Riehl (3) found

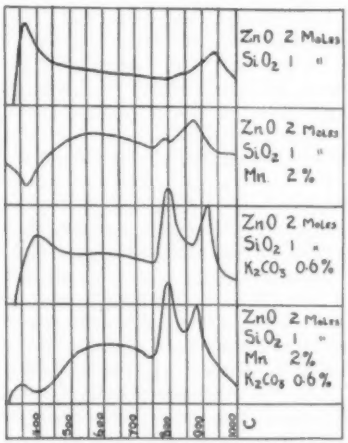

FIG. 1

a maximum below 500 C in a plot of the activity against the heating temperature. They explained this as "activation" of the silica by the zinc oxide, and the 370 C peak in the heating curve may be due to this.

The ZnO-MnO_2-SiO_2 system (Fig. 1: Second curve).—The addition of a small quantity of manganese dioxide to the reaction mixture had three effects on the heating curve. The endothermic effect with a maximum at 370 C is due to the thermal decomposition of manganese dioxide, a process which normally reaches a maximum at 530 C in air (4, 5). However, the dispersal of the oxide over the surfaces of the other reactants evidently alters the equilibrium. The shift of the exothermic peak for the zinc oxide-silica reaction, from 935 C down to 870 C, and the appearance of the small exothermic peak at 790 C are less readily explained. The 790 C peak is not due to a reaction between silica and manganese dioxide, or one of its decomposition products, for there is no indication of an exothermic peak at this temperature in the heating curve for this reaction, reproduced in Fig. 2. The major exothermic peak at 1050 C is discussed below.

Zinc oxide and manganese dioxide apparently do react together, as may

be seen from Fig. 3 in which the upper and lower heating curves relate to chemically equivalent mixtures of manganese dioxide with beryllium hy-

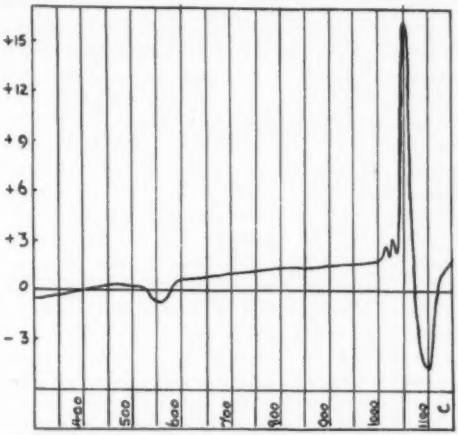

FIG. 2. Heating curve for SiO_2 with 10 per cent by weight of Mn

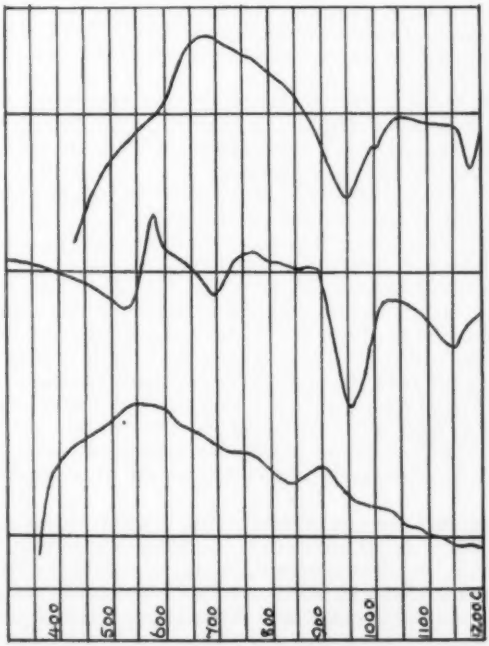

FIG. 3. Heating curves for $Be(OH)_2$-MnO_2; MnO_2 only; ZnO-MnO_2

droxide and zinc oxide, respectively. The middle heating curve is that for manganese dioxide alone. Reproduction in the upper curve of the endothermic effects at 950 C and 1180 C, very similar to the endothermic effects in manganese dioxide alone, shows that no reaction occurs between beryllium hydroxide or oxide and oxides of manganese. On the other hand, the absence of these endothermic maxima in the lower curve proves that manganese oxides combine with zinc oxide, although this combination does not produce an exothermic peak at 790 C. The colors of the various products confirm this view. The ignited beryllium hydroxide-manganese dioxide mixture had a maroon color similar to that of ignited manganese dioxide alone, whereas the final color of the zinc oxide-manganese dioxide mixture was an orange-brown. This product may be $ZnO \cdot Mn_2O_3$ which has been found as one of the products of certain dry-cell reactions (6). Further experiment showed that reaction of the orange-brown product itself with silica does not cause the exothermic peak at 790 C, but it does produce an exothermic effect similar in general characteristics to the main zinc oxide-silica reaction peak, with a shift from 935 C down to 910 C.

Another point to be mentioned here, which applies equally to the ZnO-BeO-MnO_2-SiO_2 systems, is that the remarkable exothermic peak of Fig. 2 never appears in heating curves for mixtures in which both zinc oxide and manganese dioxide are present. The extreme sharpness of this peak, together with its height, would enable its detection with considerably reduced amounts of the reactants present, but at best only a slight ripple in the heating curve is observed. This shows that the normal reactions between silica and manganese dioxide do not occur in the presence of zinc oxide, and supports the suggested prior reaction between zinc oxide and manganic oxide.

The ZnO-K_2CO_3-SiO_2 system (Fig. 1: Third curve).—The remarkable effect, produced by the inclusion of 0.6 per cent of potassium carbonate in the reaction mixture, could not be identified with any of the following reactions, studied by the same method:

(*a*) Formation of potassium silicate from K_2CO_3 and SiO_2.
(*b*) Formation of potassium zincate, K_2ZnO_2.
(*c*) Reaction between potassium zincate and silica.
(*d*) Reaction between potassium silicate and zinc oxide.

Evidence for the formation of the phase $K_2O \cdot ZnO \cdot SiO_2$ has been published recently (7), but the possible participation of this compound in the reactions under discussion has yet to be investigated.

The ZnO-MnO_2-K_2CO_3-SiO_2 system (Fig. 1: Fourth curve).—The simultaneous addition of both manganese dioxide and potassium carbonate to the reaction mixture does not involve any new reactions, and the heating curve obtained combines the effects of the two previous cases. The coincidence of the 790 C peak, due to the manganese addition, with the 795 C peak, due to the potassium carbonate, results in one peak only in the composite curve.

The ZnO-BeO-SiO_2 system (Fig. 4: First curve).—Comparison of the first curves of Fig. 1 and 4 shows that the substitution of 30 mole per cent of the zinc oxide by an equivalent amount of beryllium hydroxide produces a new exothermic peak at about 800 C. The peak due to the formation of zinc silicate still appears, at 920 C, though it is sharper.

One would expect two exothermic peaks in this case and confirmation

that the first is due to the formation of beryllium silicate was sought. The heating curve for a mixture of 2 moles of beryllium hydroxide with 1 mole of silica was obtained, and part of this curve, together with the corresponding part of the heating curve for beryllium hydroxide alone, is reproduced in Fig. 5. From the upper curve it is seen that the beryllium

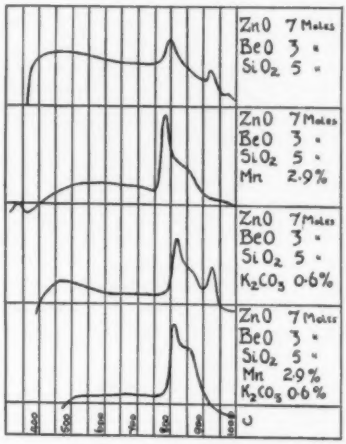

FIG. 4

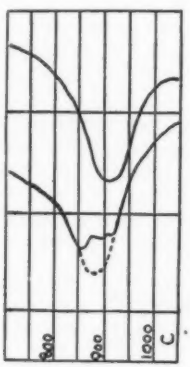

FIG. 5

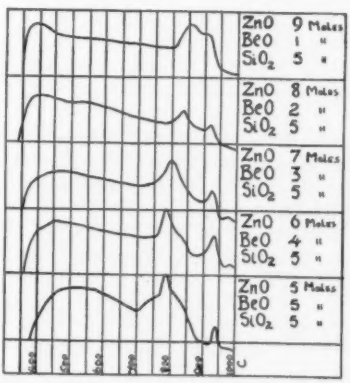

FIG. 6

oxide, formed by the decomposition of the hydroxide, undergoes some kind of endothermic change of considerable magnitude, in the temperature range 700 C to 910 C. Reference to the lower curve shows that, in the course of this change, reaction with silica begins at 850 C. The lower heating curve is the resultant of simultaneous endo- and exothermic

processes, and the exothermic peak for the formation of beryllium silicate comes at about 900 C, that is, some 100 C higher than the temperature at which the first exothermic peak occurs in the first heating curve of Fig. 4.

This indicates interaction between zinc oxide and beryllium oxide and the results given in Fig. 6 confirm this supposition. These heating curves show that, as the beryllium oxide content of the reaction mixture is increased relative to the zinc oxide content, the two exothermic peaks become more widely separated. Most of this effect is due to a progressive shift of the first peak toward lower temperatures, although there is a smaller shift of the other peak in the opposite direction.

Following up this result, an equimolecular mixture of zinc oxide and beryllium hydroxide, without any silica, was studied by thermal analysis. The heating curve gave no evidence of interaction, but it was found that the heated mixture was fluorescent when excited by the 3650 Å mercury line. Furthermore, the color of the luminescence was yellow and quite distinct from that of pure zinc oxide.

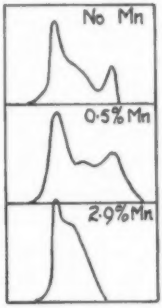

FIG. 7

There is little doubt, therefore, that a complex of zinc oxide and beryllium oxide is formed and that this complex characterizes the reactions in the ZnO-BeO-SiO_2 system, and in the more complex system containing potassium carbonate.

No evidence could be obtained by thermal analysis to support the idea that the observed reactions are exothermic exchange reactions of the type

$$2\,(ZnO \cdot BeO) + SiO_2 = Zn_2SiO_4 + 2BeO$$

$$2\,(ZnO \cdot BeO) + SiO_2 = Be_2SiO_4 + 2ZnO$$

The ZnO-BeO-MnO_2-SiO_2 system (Fig. 4: Second curve).—The effect of adding manganese dioxide to the reaction mixture is primarily the disappearance of the peak at 920 C. Whether this is due to a large shift of this peak toward lower temperatures, whereby it merges with the exothermic peaks between 800 C and 850 C, is not clear. The effect is dependent on the manganese concentration, as shown by Fig. 7, from which it can be seen that the addition of 0.5 per cent by weight of manganese does not alter the position of the peak. At the same time, a steady building up

of the exothermic peak at about 850 C is indicated, although too much may not be inferred from this because of the many difficulties besetting the use of differential thermal analysis quantitatively. There is no doubt that the zinc oxide-silica reaction is affected in a different way by the presence of manganese when beryllium oxide is also taking part.

The ZnO-BeO-K_2CO_3-SiO_2 system (Fig. 4: Third curve).—In the case of the potassium carbonate addition to the reaction mixture, the effects seem to be much the same as in the ZnO-K_2CO_3-SiO_2 system. The exothermic peak already present at 800 C is sharpened and heightened to some extent, as is the reaction peak at 920 C. A fresh effect is produced at about 850 C, similar to that already mentioned above in connection with the manganese additions. Although no satisfactory explanation of these effects has been found, the heating curves do show how the course of these solid reactions can be modified by very small quantities of substituents, so that products with different properties are obtained.

The ZnO-BeO-MnO_2-K_2CO_3-SiO_2 system (Fig. 4: Fourth curve).—Finally, the last curve of Fig. 4 shows that the simultaneous addition of manganese dioxide and potassium carbonate to the reaction mixture produces effects which combine the features of the two previous cases, as was found to be the case in the simpler system without beryllium oxide.

CONCLUSIONS

In the synthesis of zinc silicate phosphors by the dry method, there is evidence that a compound of zinc oxide and an oxide of manganese, possibly $ZnO \cdot Mn_2O_3$, is formed. The appearance of this phase in the system is associated with the disappearance of a prominent exothermic peak in the silica-manganese dioxide heating curve, and with a lowering of the reaction temperature for the formation of zinc silicate. This suggests that the manganese is incorporated in the phosphor, not by the solution of manganese silicate in zinc silicate, but by the direct formation of the double silicate.

In the case of substituted zinc silicate phosphors, in which beryllium oxide is a substituent, a complex of zinc oxide with beryllium oxide is formed in the course of the reaction. This results in a new exothermic reaction whereby beryllium silicate is obtained at a much lower temperature than normal. Alternatively, the new reaction is the direct formation of the double silicate of zinc and beryllium. This would help to explain the color changes in the fluorescence, referred to in the introduction to this paper, for if, in the early stages of reaction, there is formed a beryllium-rich silicate into which further zinc oxide is subsequently incorporated, the color of the fluorescence would shift in the direction from red to yellow.

In zinc silicate phosphors in which potassium is a substituent, the presence of the potassium carbonate, even in small quantity, has a considerable effect and causes new exothermic reactions of a very sharp and distinctive character. These effects remain in the presence of other substituents, including manganese dioxide and beryllium hydroxide or oxide The precise nature of these new reactions has not yet been established, but an inference of some connection between them and the improved stability of the products under operating conditions seems well founded.

The reactions between oxide components other than silica, which have not been discussed hitherto in connection with these phosphors, explain why the products obtained by omitting one or more of the reactants in the initial stages of reaction differ from those obtained in the ordinary way. In view of the ability of zinc oxide to form compounds or complexes with the other basic oxides, the particular effect of withholding it in the earlier stages can be better appreciated.

The usefulness of differential thermal analysis in revealing the unsuspected reactions, and, thereby, suggesting alternative ways of carrying out the processes of phosphor synthesis, are well illustrated by the results of this investigation.

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